

South Dakota State University

Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange

Electronic Theses and Dissertations

1972

Nitrate Movement in Freezing or Frozen Soils

Donald G. Moore

Follow this and additional works at: <https://openprairie.sdstate.edu/etd>



Part of the [Plant Sciences Commons](#)

Recommended Citation

Moore, Donald G., "Nitrate Movement in Freezing or Frozen Soils" (1972). *Electronic Theses and Dissertations*. 5431.

<https://openprairie.sdstate.edu/etd/5431>

This Dissertation - Open Access is brought to you for free and open access by Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. For more information, please contact michael.biondo@sdstate.edu.

LIBRARY
MAY 1972
20

NITRATE MOVEMENT IN FREEZING OR FROZEN SOILS

BY

DONALD G. MOORE

A thesis submitted
in partial fulfillment of the requirements for the
degree Doctor of Philosophy, Major in Plant Science,
South Dakota State University

1972

NITRATE MOVEMENT IN FREEZING OR FROZEN SOILS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Doctor of Philosophy, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser

Date

Head, Plant Science Dept.

NITRATE MOVEMENT IN FREEZING OR FROZEN SOILS

Abstract

Donald G. Moore

Under the supervision of Dr. E. M. White

Nitrate movement in freezing and frozen soils was studied in both disturbed and undisturbed soils by laboratory and field investigations. Thermoelectric cooling plates were placed in insulated freezing boxes. Soil cores placed in the freezing boxes were stored, frozen, or thawed at a specific temperature or temperature gradient. Field plots and soil columns reset into the field environment were used to observe migration of either fall- or winter-applied nitrate.

Movement of surface applied nitrate was caused by passage of a freezing front through either saturated or unsaturated sand or saturated Vienna loam. The nitrate movement due to freezing was greater in unsaturated sand than in saturated sand possibly due to the formation of more brine pockets in the saturated sand. Movement of nitrate from the surface of different kinds of clay-sand mixtures maintained at -5°C was influenced by clay type, kind of exchangeable cation, and soil moisture content. Negative adsorption of nitrate by clay surfaces and the formation of thin ice lenses which interrupted liquid-film continuity probably were the major factors affecting nitrate movement. Nitrate applied to a frozen, saturated Kyle clay or Vienna loam moved more when it was applied to the -0.5°C rather than the -3.3°C soil-column end. This difference was not found for Egeland sandy loam. In

an experiment with freezing and thawing Vienna-loam columns nitrate moved with water toward the concentrated (warm) end of the core during the thaw cycle. Fall-applied nitrate moved more than winter-applied nitrate in soil cores for two separate years in the field studies. Nitrate appeared to have moved down to a 30-cm depth in the field plots after either a fall or winter nitrate application.

Mechanisms for nitrate movement in addition to salt rejection from the ice in the freezing soil solution, movement with mass flow of water, and diffusion due to concentration gradients could be caused by the Soret effect and brine-pocket migration.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. E. M. White, Professor of Soil Science, for his guidance and support in the preparation and presentation of this study.

Dr. Lee Tucker, Experiment Station Statistician, and Paul Evenson, Assistant Professor of Plant Science, are gratefully acknowledged for their assistance with the statistical analyses and instrument use, respectively.

This thesis is dedicated to my loving wife, Sandra, and two sons, Michael and Martin, who provided incentive and much understanding necessary for the undertaking and completion of this study.

Financial aid was provided through the Plant Science Department at South Dakota State University by a National Defense Educational Act Fellowship.

TABLE OF CONTENTS

	Page
ABSTRACT	iii
ACKNOWLEDGMENTS	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	viii
LIST OF TABLES	x
INTRODUCTION	1
REVIEW OF LITERATURE	2
A. Unfrozen Water in "Frozen Soils"	2
B. Continuity of Water Films and Water Movement	7
C. Salt Movement in Frozen Soils	11
EXPERIMENTAL MATERIALS AND PROCEDURES	16
A. The Controlled Freezing Apparatus	16
B. Preparation of Soil Columns	21
C. The Field Experiment	24
D. Soil Sampling and Analysis	26
METHODS FOR INDIVIDUAL EXPERIMENTS	29
A. Laboratory	29
1. Passage of a freezing front through a saturated sand column	29
2. Freeze-thaw cycles in a saturated Vienna-loam soil .	30
3. Nitrate distribution after a freeze-thaw cycle with nitrates applied to the end that was not frozen	31
4. Nitrate movement in a sand or clay-sand mixture at -5 C	32

5. Nitrate movement in frozen saturated soils that were subjected to a temperature gradient	34
6. Others	35
B. Field	36
1. Year 1 — Nitrate distribution after fall or winter application	36
2. Year 2 — Nitrate distribution after fall or winter application	36
RESULTS AND DISCUSSION	38
CONCLUSION	55
BIBLIOGRAPHY	58
APPENDICES	62

LIST OF FIGURES

FIGURE	Page
1. Unfrozen water contents in typical nonsaline soils	3
2. The change in d(001) spacings, for Wyoming bentonite saturated with various cations, during the warming portion of a freeze-thaw cycle	4
3. Unfrozen water content in kaolinite and montmorillonite clays with different exchangeable cations	5
4. Lattice collapse and re-expansion of sodium-bentonite during a freeze-thaw cycle	6
5. Environmental control chambers (ECC) used for laboratory investigations	16
6. ECC-A containing drill holes for placement of core samples	16
7. ECC-B interior construction and instrumentation	17
8. Aluminum heat-flux plate for two-directional use	18
9. Coolant source for thermoelectric heat flux plates	19
10. Temperature control and monitors for ECC	20
11. Tubing used for diffusion-column containers	21
12. Apparatus used for obtaining undisturbed soil cores	22
13. Packing apparatus for high pressure packing	23
14. Pressure cookers and controls used to desaturate soils to a desired moisture tension	24
15. Experimental arrangement of year-one field experiment	25
16. Cover used for year-one field experiment	25
17. Nitrate analysis equipment	28
18. Distribution of nitrate ions in either frozen or unfrozen sand columns	38

19.	Nitrate distribution in sand and clay-sand mixtures used in Exp. A-4 when column temperatures were held at ≈ -5 C for a 3-week duration	44
20.	The DN interaction means for Exp. B-1.	49
21.	Means for the DT interaction in Exp. B-2a	51

LIST OF TABLES

TABLES	Page
1. Nitrate means (ppm $\text{NO}_3\text{-N}$) for Exp. A-2 involving multifreezing of a saturated Vienna-loam soil	40
2. Nitrate distribution (ppm $\text{NO}_3\text{-N}$) with depth after either a freeze or freeze-thaw cycle in Vienna-loam soil either at 0 or 0.34 atm of moisture tension with nitrates applied to the warm end of the column	42
3. Fraction of nitrates in the 1- to 10-cm depth to total in the core for sand and clay-sand mixtures maintained at -5 C for 3 weeks	45
4. Nitrate content means (ppm $\text{NO}_3\text{-N}$) for the PDS interaction in Exp. A-5	47
5. Nitrate means (ppm $\text{NO}_3\text{-N}$) for the DPM interaction in Exp. B-2b	52
6. Nitrate means (ppm $\text{NO}_3\text{-N}$) for the DTS interaction in Exp. B-2b	53
7. Nitrate (ppm $\text{NO}_3\text{-N}$) distribution for Exp. B-2c	54

INTRODUCTION

Nitrate movement in soils during the fall and winter could be affected by soil temperature and temperature-gradient fluctuations. In colder regions lacking permafrost the soil freezes from the surface downward in the fall. The frozen layer may remain frozen during the winter or the upper part may freeze and melt several times. As the soil water freezes, it may form ice crystals in place or it may move to a lens of ice in the soil. Because the freezing temperature is usually above the eutectic temperature of the soil solution, water tends to segregate and freeze in the pure state. The soluble salts in the soil solution accumulate in the unfrozen water and form a relatively concentrated brine or precipitate if their solubility is exceeded.

In early experiments, Bouyoucos (1917) demonstrated that part of the soil water remains unfrozen at temperatures below the normal freezing point of water. This unfrozen liquid, if present in continuous films around and between mineral grains, is a path for the migration of soluble salts. Transport mechanisms that could be involved are: diffusion due to concentration gradients, movement with mass flow of water, gravity flow of brine pockets, and ionic movement associated with temperature induced ion-activity gradients (other than thermally induced water flow).

Laboratory and field investigations with disturbed and "undisturbed" soil materials were conducted: 1) to determine if nitrate movement results from unidirectional freezing of soils and 2) to determine if nitrate movement occurs in frozen soils.

REVIEW OF LITERATURE

A. Unfrozen Water in "Frozen Soils"

Investigators have used different methods (i.e., dilatometer, calorimeter, X-ray diffraction, differential thermal analysis) to determine the unfrozen water content in frozen soil materials (Hemwall and Low, 1955; Kolaian and Low, 1963; Nerseova (also spelled Nersesova) and Tsytovich, 1963; Anderson and Hoekstra, 1965; Anderson, 1966; Anderson and Tice, 1971). These different scientists report the existence of unfrozen water in frozen soils but do not agree on the quantity of unfrozen water present.

The most comprehensive unfrozen-water-content data were presented by Nerseova and Tsytovich (1963). The contents were determined calorimetrically and reported as unfrozen water, as percent of the dry-soil weight, at a given temperature (T -degrees centigrade). As the surface area of soil material increases (1 through 5 - Fig. 1) the quantity of unfrozen water at a given temperature increases.

Anderson (1968) characterized interfacial regions in frozen soils as "ice-ice (II; grain boundary), ice-water-air (IWA), silicate-water-silicate (SWS; primarily interlamellar), and silicate-water-ice (SWI; extralamellar)". He suggested that the IWA, SWI, and SWS interfaces include a liquid-like water layer in contrast to the II surface.

Jellinek (1967) presented a survey of 100-years controversy as to the existence of a liquid-like transition layer on ice (IWA). He

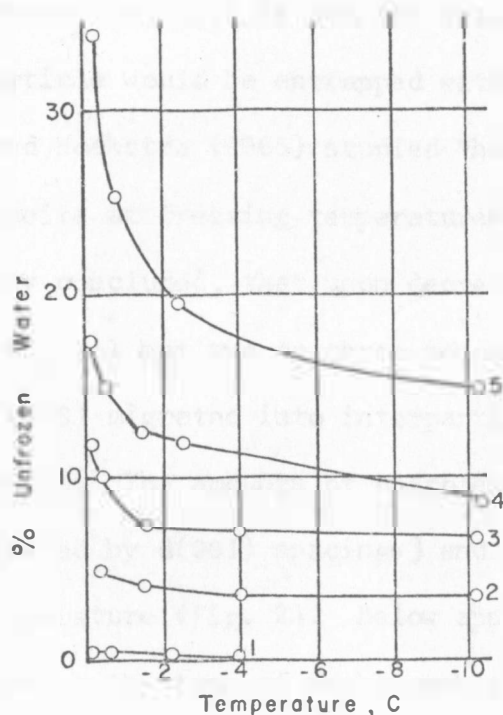


Fig. 1 — Unfrozen water contents in typical nonsaline soils: (1) quartz sand, (2) sandy loam, (3) loam, (4) clay, and (5) clay containing montmorillonite (Nersecva and Tsytoich, 1963).

concluded that a liquid-like layer is very likely to exist and may vary from a maximum thickness of 100 Å near the melting point until it vanishes at about -30°C .

Hoekstra and Miller (1967) demonstrated the migration of glass beads through ice that was subjected to a temperature gradient. A liquid layer (SWI) surrounding the bead allows water flow from the warm to the cold side of the bead where the water freezes. This process causes the bead to migrate through the ice. Corte (1962, 1963) observed size sorting of particles in a heterogeneous mixture during the advancement of an ice-water interface. Movement of particles at the freezing front requires the presence of a liquid-like

layer (SWI) between the particle and the ice. If it were not present, the particle would be entrapped within the ice.

Anderson and Hoekstra (1965) studied "homoionic", clay-water pastes of Wyoming bentonite at freezing temperatures using X-ray diffraction techniques. They concluded, that upon decreasing temperatures to a subfreezing level, all but two or three monomolecular layers of interlamellar water (SWS) migrated into interparticle pore spaces where it crystallized as ice. The amounts of unfrozen interlamellar water were estimated [indicated by $d(001)$ spacings] and shown to be primarily dependent on temperature (Fig. 2). Below approximately -5°C very little dependence on the type of exchangeable cation was noticed. The $d(001)$ spacings were nearly independent of initial water content.

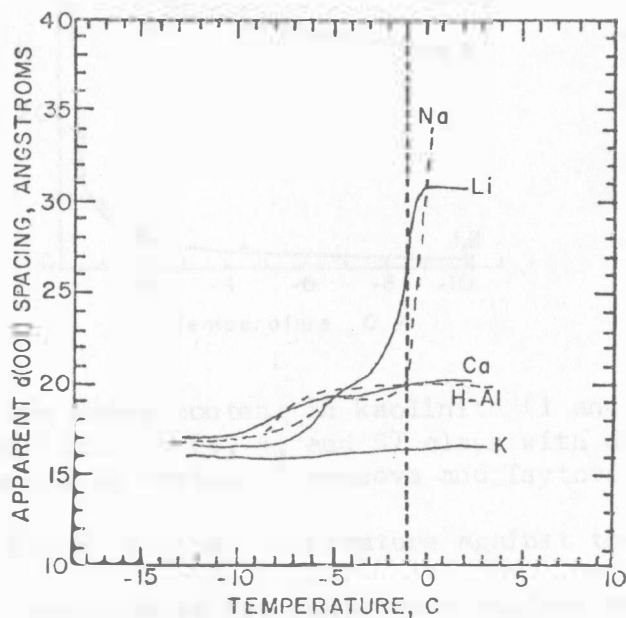


Fig. 2 — The change in $d(001)$ spacings, for Wyoming bentonite saturated with various cations, during the warming portion of a freeze-thaw cycle. The dotted line indicates the temperature at which ice was last known to be present (Anderson and Hoekstra, 1965).

Using calorimetric studies of calcium or sodium ascangel-bentonite or kaolinite clays, Nerseova and Tsytoovich (1963) found that the influence of exchangeable cations on the amount of water in liquid phase was small compared to the influence of the surface properties of the clays (Fig. 3).

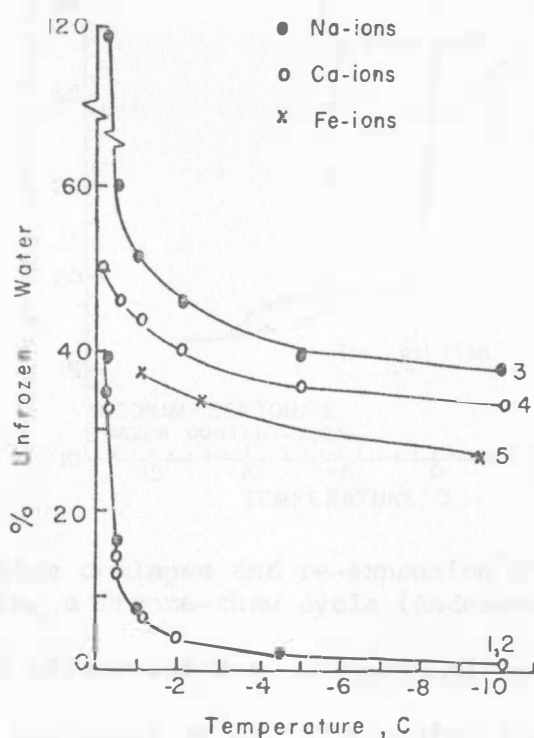


Fig. 3 -- Unfrozen water content in kaolinite (1 and 2) and montmorillonite (3, 4, and 5) clays with different exchangeable cations (Nerseova and Tsytoovich, 1963).

Anderson (1968) plotted temperature against the ratio of total unfrozen-water contents to the respective surface areas for montmorillonite and kaolinite. He observed, that above -5 C, kaolinite possessed a thicker surface liquid-like layer than the montmorillonite clays. From -5 to -10 C they were essentially the same. From this

type of data it appears that the SWI interface may be thicker than the SWS interface at temperatures down to about -5°C .

Anderson and Hoekstra (1965) observed hysteresis associated with the migration of water between interlamellar and interparticle spaces (Fig. 4).

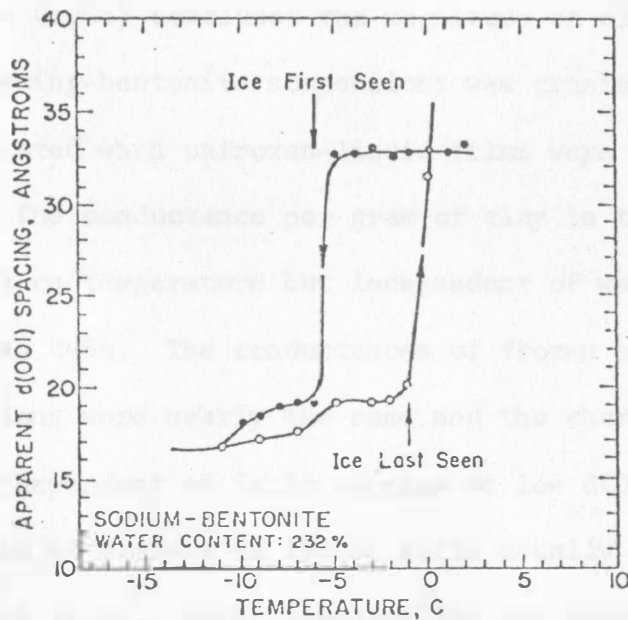


Fig. 4 — Lattice collapse and re-expansion of sodium-bentonite during a freeze-thaw cycle (Anderson and Hoekstra, 1965).

They felt the effect was due to supercooling since if the sample were artificially nucleated at -1.5°C the d(001) spacing decreased so that the cooling and warming curves nearly coincided.

B. Continuity of Water Films and Water Movement

Liquid-water and/or ion movement can occur if a potential for movement exists and if continuous liquid films are present within the media. This section will present evidence for the presence of continuous films and the migration of liquid water.

Hoekstra (1965) concluded the magnitude of electrical conductance of frozen Wyoming-bentonite suspensions was consistent with theoretical values calculated when unfrozen-liquid films were assumed to be continuous. The conductance per gram of clay in the frozen suspension was dependent on temperature but independent of water content in the range of 56 to 346%. The conductances of frozen sodium- or calcium-clay suspensions were nearly the same and the charge mobility was apparently independent of ionic species at low $d(001)$ spacings.

Migration of cations in frozen soils usually requires the presence of liquid-like films. Both interlamellar and extralamellar surfaces would transport cations. Murrmann, Hoekstra, and Bialkowski (1968) determined the self-diffusion coefficient of sodium ions in Wyoming bentonite at various subzero temperatures. They concluded the observed rapid diffusion over a 5-cm distance at -15°C would not be possible unless water films were both present and continuous. Thus the continuous films of extralamellar liquid water were important for diffusion over this distance. The self-diffusion coefficients probably decreased with decreasing temperature because the liquid-film thickness decreased.

Observations of electro-osmotic migration of liquid water in frozen Wyoming bentonite led Hoekstra and Chamberlain (1964) to conclude

that liquid water was transported through continuous films. As water moves to the cathode ice melts to replenish the water in the liquid film. Therefore, if ice is present the liquid-film thickness is controlled by temperature.

Hoekstra (1966) measured moisture movement to a freezing front in unsaturated Fairbanks silt. He concluded that an ice phase enhances moisture transfer to the cold side. Moisture movement within the frozen zone, which was too large to occur in the vapor phase, probably occurred in the liquid phase along continuous films. The rate of migration decreased rapidly as temperature decreased below 0 C. Koopmans (1965) indicated that water may move through small soil pores containing liquid-like water but this would only be significant in the temperature range from 0 to -0.2 C.

Hoekstra (1969) measured the pressure developed during freezing of granular- and clay-type soils. He summarized that in clay soils the pressure developed depends on the temperature at the ice lens whereas in granular soils the pressure is independent of temperature. For ice lenses to grow water must migrate to the lenses. As ice lenses grow, the minerals are separated so the unfrozen water films are no longer continuous paths for water migration. In a frozen unsaturated granular soil, the ice usually is discontinuous and flow can occur in the films (Hoekstra, 1966). Many microscopic ice lenses may extend across pores in a saturated soil and impede water movement. The large amount of unfrozen water in clay-type soils provides many films for liquid migration. Thus, Hoekstra's (1969) observation that pressure developed was temperature dependent probably is related to the soil's

capability to transport water to the freezing front for ice lens growth.

Dirksen and Miller (1966) observed moisture flow to a freezing front and within the frozen zone. By comparing calculated values for vapor transport with observed values of moisture migration in a moist-unsaturated soil, they concluded that the largest volume of moisture flow to the freezing front was attributed to hydraulic (liquid) rather than thermal (vapor) transport. Therefore, after an ice phase forms, a hydraulic gradient is present for water movement. As ice ceases to form, thermal movement would contribute a greater proportion of the total movement. In their closed system this involved vapor transport to the cold end and liquid transport to the warm end. They observed moisture migration into the frozen zone and attributed this to the frozen soil imbibing water as the thickness of films decreased with temperature.

Ferguson, Brown, and Dickey (1964) found in a field study that no appreciable water moved into the frozen zone during the winter if the subsoil water tension was greater than 5 bars. Willis et al. (1961) reported in North Dakota that overwinter freezing had little, if any, effect on the accumulation of water at the depth of freezing. However in an area with a high water table, Willis et al. (1964) found that a decrease in the water-table height occurred as soil water increased in the frozen zone. Sartz (1968) found in field studies that infiltration and percolation were the primary mechanisms of water movement into the frozen zone where groundwater tables were at least 5 m below the ground surface. Cary (1966) calculated that vapor transport in a natural soil system could not be great enough to explain

observations reported in the literature for water movement into the frost zone.

C. Salt Movement in Frozen Soils

Surface applied salts may be transported by various mechanisms during soil freezing and after the soil has frozen. Sections A and B of this manuscript presented evidence for the presence of unfrozen, continuous liquid-like films in partially frozen soil systems. This section will outline mechanisms for salt movement during freezing and within the frozen zone.

Freezing forms relatively pure ice thereby concentrating salt in the remaining solution. The solution salts may either concentrate in brines or precipitate. Movement of salt can be in all directions except into the ice. One of these directions is downward away from the freezing front. This illustrates the first mechanism of salt movement presented.

Diffusion along salt concentration gradients and salt movement with mass flow of water are two other possible mechanisms for ion movement. Fick's first law states that the flux of a substance through a plane perpendicular to the direction of diffusion is directly proportional to the concentration gradient. The proportionality constant is termed the diffusion coefficient. Nitrate movement with mass flow of water in a noninteractive system can be described as the flux equal to the quantity of water translocated multiplied by the concentration of nitrate in that water. Many soil properties affect these mechanisms. Gardner (1965) stated that the diffusion coefficient could fluctuate with viscosity of the diffusing medium, tortuosity of the diffusion path, temperature, concentration of electrolyte, type of counterions present, soil-moisture content, soil reaction, and others.

Kemper (1960) applied diffuse-double-layer theory to describe experimental observations of the salt-sieving effect. The effect of negative adsorption of anions to the negatively charged clay platelets was to restrict moisture movement by 90% in a relatively dry clay-type soil. Van Schaik and Kemper (1966) found a 50% reduction in the chloride diffusion coefficient in sodium- or calcium-saturated bentonite and attributed this to effects caused by negative adsorption due to a wide range in pore sizes.

Liquid-water movement in thin films creates a viscous drag on cations located near the clay surface. The anions are repelled from the clay surface and are not able to diffuse freely through small pores between clay particles, thus creating a salt-sieving effect. As cations are moved with the flow of water a streaming potential is developed. The streaming potential tends to reverse the direction of cation flow and increase anion movement in the direction of water flow. Because the charge due to cations in many soil systems is much larger than the charge due to anions (excluding negatively charged colloidal materials), the net effect of salt sieving and streaming potentials in a relatively dry system is to reduce the rate of both liquid and anion flow. Nielson et al. (1970) suggest that when the film thickness approaches the thickness of the diffuse layer of adsorbed cations (20 to 300 Å) that solute movement may be restricted.

Edwards, Posner, and Quirk (1965) found that the distance chloride was excluded from monovalent-cation Fithian-illite clay surfaces decreased with decreasing cation hydration. The calcium illite did show some negative adsorption but magnesium and aluminum illites

showed positive adsorption. Negative adsorption was greater for expanding than nonexpanding clays.

Porter et al. (1960) observed a decrease in the diffusion transmission coefficients in unsaturated soils in the sequence of loam>silty clay loam>clay. The coefficient increased for each texture as moisture content increased. One of the factors that could have caused this increase is that as soil-water content increases, the thickness of films connecting larger pores increases and the salt-sieving effect is reduced.

Anions tend to be excluded from a portion of the total volume occupied by solution. For a specific soil an increase in water content dilutes the electrolytes and increases the magnitude of negative adsorption (Babcock, 1963). Thomas and Swoboda (1970) concluded that in a high versus low cation-exchange-capacity soil the effect of anion exclusion in the high cation-exchange-capacity soil increased the efficiency of chloride movement relative to total water movement during leaching. They observed that the efficiency decreased from 137 to 112% by increasing electrolyte concentration from 0.01 to 1.0 N.

As the soil freezes, concentrated brine pockets may form. The concentrations of the brine solution at a given temperature are determined by the solubility of the salts. If a temperature gradient exists across the brine pocket, concentration gradients usually exist. The driving force for the movement of brine pockets is the difference in composition between the warm and cold sides of the pocket. Hoekstra, Osterkamp, and Weeks (1965) used a simple diffusion model

to calculate migration values of ice-imbedded potassium-chloride or sodium-chloride brine pockets. Comparisons of calculated with observed values were consistent but the observed were always less than the calculated. Neither the gravitational field or crystallographic orientation had a significant effect on movement. Kingery and Goodnow (1963) evaluated the mechanisms of brine pocket migration through sea ice. They concluded that gravity drainage through grain-boundary channels was the primary mechanism with temperature-gradient diffusion mechanisms as secondary.

Lewis and Walker (1970) observed a gradual increase in salinity of sea water beneath the ice during the winter in Cambridge Bay. They concluded that as the thickness of ice increased, salt rejection concentrated salt in the under-lying water. Temperature anomalies measured in the water beneath the ice suggested that salt-rich streamers were falling from the ice-water interface.

Fay (1920) defined the "Soret Effect" as:

"That principle by which if differences of temperature are induced in a solution of common salt or other substance in water, the dissolved material will become relatively concentrated in those portions in which the temperature is the lowest".

Snowdon and Turner (1960) measured values of the Soret coefficient (S):

$$S = -(1/m)(dm/dT)$$

where m = molality and T = temperature (degrees Kelvin).

The Soret coefficient for sodium nitrate in 0.01 N aqueous solutions at 25 C was 1.27×10^{-3} /C. The positive value indicates the solution concentrates on the colder side. For a detailed theoretical

development of the Soret effect refer to the text by de Groot and Mazur (1962). Cary and Mayland (1972) observed salt migration in a frozen silt-loam soil subjected to a temperature gradient of 5 C (-5.5 to 0.5 C) in 24 cm. They concluded that high soil-moisture contents and soluble salts with positive Soret coefficients favored salt and water movement to the cold surface. Up to a three-fold change in salt concentration from cold to warm ends was observed after a 6-week-time interval.

Campbell, Ferguson, and Warder (1970) reported from a winter field-study in Canada that both nitrate and moisture moved upwards in a frozen soil at field capacity and that at the wilting percentage the movement was negligible. Murrmann and Hockstra (1970) observed that self-diffusion coefficient for sodium ions in frozen Wyoming-bentonite suspensions decreased rapidly with decreasing temperature. They attributed this to liquid film reduction. They determined that a temperature gradient up to 0.3 C/cm had little effect on either sodium-ion diffusion or water movement over a temperature range of 0 to -12 C.

EXPERIMENTAL MATERIALS AND PROCEDURES

A. The Controlled Freezing Apparatus

Laboratory apparatus for freezing was developed so that the heat-flux direction within cores was substantially controlled. Environmental-control chambers (ECC) with insulated walls were constructed to house the heat-flux equipment and samples (Fig. 5).



ECC-A



ECC-B

Fig. 5 — Environmental control chambers (ECC) used for laboratory investigations.

The ECC were in turn housed in a walk-in cold chamber ($\approx 4^\circ\text{C}$) for ambient temperature control. Heat flux between cores was controlled by placing the cores in holes drilled in styrofoam (Fig. 6).



Fig. 6 — ECC-A containing drill holes for placement of core samples.

An example of apparatus arrangement and sample positioning used is illustrated in Fig. 7.

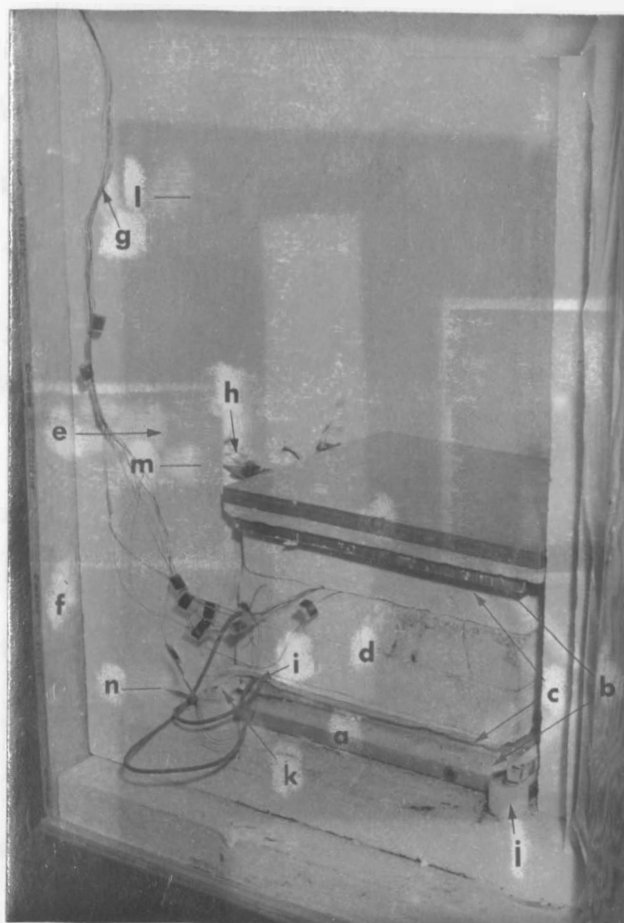


Fig. 7 — ECC-B interior construction and instrumentation.

- a. Cambion Model 582-7245-01¹ 120-watt water-cooled thermoelectric cooling plate² (25.4x30.5 cm cooling surface)

¹Product name and model number specified only for the reader's procurement of further specifications of unusual equipment and does not indicate an endorsement by either the author or South Dakota State University.

²Cambridge Thermoionic Corporation, 445 Concord Avenue, Cambridge, Massachusetts.

- b. Aluminum heat-transfer plates (1.3x25.4x30.5 cm)
- c. Thermal contact compound (Silicone loaded with zinc oxide)
- d. Styrofoam core-sample insulation
- e. 10-cm styrofoam wall
- f. Outside support frame (1.3-cm exterior plywood)
- g. 24-gauge copper and constantan Type-T wires for thermocouple leads and junctions
- h. Access port to (a) for water inlet and outlet hoses
- i. Sensor and temperature-control probes for cold plate
- j. Wooden support pegs through styrofoam (asbestos layers on ends)
- k. Steel support arm from heat-transfer plate (asbestos insulation at contact)
- l, m, or n. Water-line access locations.

Two sets of six cores, which were separated by either a plate of styrofoam insulation or a hollow aluminum flux plate at location (m), could be frozen with two equitemperature freezing plates located at locations (l) and (n). The heat flux across either side of the aluminum plate should have been equal if the temperature differentials were equal. Figure 8 illustrates the exterior view of the aluminum plate.



Fig. 8 — Aluminum heat-flux plate for two-directional use.

ECC-A (Fig. 6) was designed so one styrofoam section of cores could be treated at the top or bottom by any combination of the three heat-flux plates.

The coolant for the thermoelectric plates was water which was circulated from a polyethylene barrel. Figure 9 illustrates the constant-temperature water supply and circulating pump. Weight-controlled micro-switches were incorporated within the coolant circulation system so if a malfunction occurred, the system's power would be terminated.



Fig. 9 — Coolant source for thermoelectric heat flux plates.

- a. Circulating pump (at least 1 liter/minute under load)
- b. Polyethylene water barrel (\approx 130 liters)
- c. ECC-B.

The aluminum-plate temperature was controlled by an 8-liter variable-temperature water bath and circulating pump.

Power was supplied to the thermoelectric plates with either a Cambion Model 809-7264-02 or Model 583-7230-01 variable DC solid-state power supply (Fig. 10).

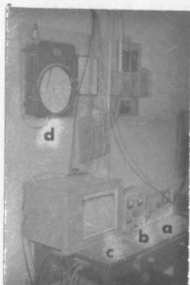


Fig. 10 — Temperature control and monitors for ECC.

- a and b. Variable DC solid-state power supplies
- c. Multipoint recorder for thermocouple sensor temperatures
- d. Continuous recorder monitoring walk-in-cold-chamber temperature.

Power supply (a) controlled the thermoelectric cold-plate temperatures to ± 0.5 C when used in conjunction with sensor and temperature probes (I-Fig. 7). Power supply (b) controlled the plate heat-flux by a manual amperage control. Two plates could be connected in series and operated from one power source.

The 24 channels of temperature data were recorded at hour intervals with a recording potentiometer in conjunction with thermocouple sensors. Thermocouples were inserted into the soil in holes formed by pushing a needle through small access holes in the tubing. The thermocouples were pushed tightly into the soil (≈ 1.5 cm from the wall) and the holes in the tube were filled with RTV-adhesive. Cold-chamber temperatures were continuously recorded on the line recorder (d).

B. Preparation of Soil Columns

Kyle clay, Vienna loam, Egeland sandy loam, grade 0 silica sand,³ and calcium- or sodium-saturated montmorillonite (Montmorillonite No. 26 - Clay Spur, Wyoming) or kaolinite (Kaolinite No. 4 - Oneal Pit - Macon, Georgia)⁴ soil materials were used as diffusion columns.

Tubing used for the diffusion-column containers was either polyethylene⁵ or glass (Fig. 11).

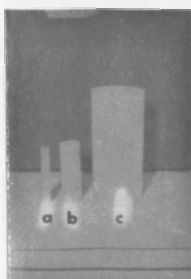


Fig. 11 - Tubing used for diffusion-column containers.

- a. Glass - 1-cm inside diameter (I.D.) by 10 cm
- b. Polyethylene - 2.5-cm I.D. by 10 cm (also 5 cm length used but not shown in photograph)
- c. Polyethylene - 7.6-cm I.D. by 18 cm.

Polyethylene tubing had rigidity and thermal characteristics desirable for handling soil cores and for unidirectional freezing. A planar freezing front was observed visually and inferred from temperature measurements in soil with variable water contents when placed in

³Gopher State Silica, Inc., LeSueur, Minnesota.

⁴Ward's Natural Science Establishment, Inc., P.O. Box 1712, Rochester, New York.

⁵Bel-Art Products, Pequannock, New Jersey.

polyethylene tubing. Visual observations were conducted at the time of sampling. Temperatures were monitored at both the soil-tube interface and center of the columns.

Glass tubing was sliced into 0.8-cm lengths. Ten 0.8-cm lengths were assembled into 10-cm cores by wrapping the spaced lengths with two layers of Parafilm "M" and taping them in place with water-resistant tape. This construction provided insulation between each length and facilitated equal increment sampling.

Undisturbed surface soils (0-18 cm) were collected in the 7.6-cm tubes (c-Fig. 11) by hydraulically forcing a steel-sheathed core in a soil area that had the surface organic debris removed (Fig. 12).

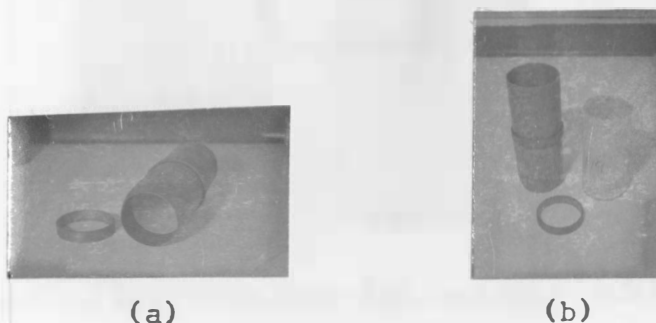


Fig. 12 — Apparatus used for obtaining undisturbed soil cores.

- a. Polyethylene tube (7.6-cm I.D.) inserted into metal sheath
- b. Coring tool and core prepared for storage.

Samples were collected the last two weeks of October 1970. If large roots or channels were visible, the cores were discarded. The core ends were covered with Parafilm "M" that was held in place by Scotch tape. Cores were stored at ≈ 4 C until used.

Bulk samples of disturbed surface soils were collected at the same time as the cores. They were air dried, crushed to pass a 1-mm

round-hole screen, and stored. Vegetation on the soil at the time of sampling was: Kyle clay—grassland, Vienna loam—alfalfa-grass mixture, and Egeland sandy loam—alfalfa-grass mixture.

The dry disturbed soils were placed in tubes by spooning approximately a 2-cm depth of soil into the container and tapping the side until noticeable settling had ceased. The sand was packed into the 7.6-cm I.D. cores by compacting (with the sand at a given moisture level) hydraulically with 1810 kg pressure (Fig. 13). The total column length was compacted at the same time to assure particle contact and to avoid layered conditions.

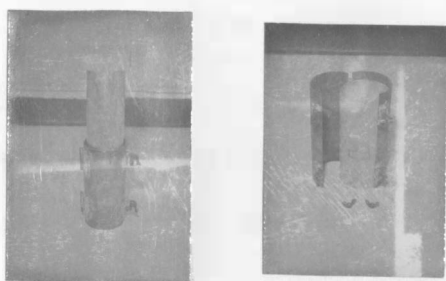


Fig. 13 — Packing apparatus for high pressure packing.

Clay-sand mixtures were placed in the glass tubing at a given moisture level by hand compacting with a rod.

The soil columns (all except those packed at specific moisture contents) were then saturated under reduced air pressure. Saturation was accomplished by capillary rise from the bottom of the soil core placed on a porous plate. Pressures up to 1.02 atm were imposed upon the system for desaturation to the desired moisture tension. Figure 14 illustrates the pressure containers and controls.



Fig. 14 — Pressure cookers and controls used to desaturate soils to a desired moisture tension.

Nitrate treatments were then applied using the appropriate quantity of saturated calcium- or sodium-nitrate solution. The cores were sealed by taping Parafilm "M" over the ends.

C. The Field Experiment

Prepared cores were reset in the field environment either before the soil froze in the fall or after the soil was frozen to at least 18 cm.

Year 1. The equivalent of 570 kg/hectare of $\text{KNO}_3\text{-N}$ was applied to either 7.6-cm I.D. cores or 30.5-cm-square plots on the Vienna-loam soil. The open cores (no covering on either the top or bottom) were buried in styrofoam blocks in a clipped alfalfa field (Fig. 15). The soil in the bottom of the core was in contact with the underlying soil. The plots were covered with a dome-shaped water-proofed canvas (Fig. 16). A polyethylene sheet extended from the surface to at least a 60-cm depth along the perimeter of the canvas cover. No soil temperatures were taken. The 30.5-cm-square plots were sampled with the

apparatus illustrated in Fig. 12.



Fig. 15 — Experimental arrangement of year-one field experiment.



Fig. 16 — Cover used for year-one field experiment.

Year 2. Cores were prepared by covering both ends with Parafilm "M" to obtain a closed system. They were then set into styrofoam blocks that were placed in a corn field prepared by surface organic-debris removal. In addition to the disturbed soils in cores, four 1.5-m-square field plots were used to study nitrate movement in undisturbed soil. Temperatures were

monitored at various times throughout the season on the warmest winter days (App. G-d). Field plots were sampled using a 2.5-cm-diameter auger.

D. Soil Sampling and Analysis

Soils were sampled from both frozen and unfrozen cores by increments of depth from the surface. Frozen cores were sliced by pounding a large knife through the material. Sampling-depth errors were small except in close proximity to the freezing front where in a few cases sampling error was up to an estimated 0.25 cm. The samples were either air-dried for nitrate analysis or oven-dried at 105 C for gravimetric moisture determination. The air-dried samples were crushed to pass a 1-mm screen.

Nitrate analyses were conducted using an Orion Model 92-07 Nitrate Electrode in conjunction with a sleeve-type Ag-AgCl reference electrode and an Orion Model 407 Specific Ion Meter.⁶

Various investigators have obtained reliable results for electrochemical determinations of nitrate (Bremner, Bundy, and Agarwall, 1968; Potterton and Shultz, 1967; Dahnke, 1971; Mahendrappa, 1969; Onken, Sunderman, and Jones, 1970; Oien and Selmer-Olsen, 1969). The following procedures were derived from their reports for use in this experiment:

1. Calibrations at the beginning of each day were conducted using 1, 10, and 100 ppm solutions of $\text{KNO}_3\text{-N}$ to determine the temperature-compensation adjustment level.
2. Recalibration after each group of 12 samples was conducted

⁶Orion Research Incorporated, 11 Blackstone Street, Cambridge, Mass.

using the 10 ppm standard.

3. Ten (10.0) grams of air-dried soil (crushed to pass a 10-mesh screen) were extracted with 25 ml of distilled water by mechanically shaking the suspension in a 50-ml stoppered flask for at least one-half hour.
4. The soil and solution were transferred into a 25-ml beaker for analysis.
5. The rinsed and blotted electrodes were immersed into the magnetically stirred suspension.
6. Direct concentrations were read from the logarithmic scale after electrode-suspension equilibrium was established (at least 1 minute or when the potential remained stable).
7. If solution concentrations were too high for the scale readings, dilutions were made by rinsing the extractant flask with an additional 50 ml of water and combining this with the original extracting solution (if further dilution was necessary the sample size was reduced to 1 g).
8. Concentrations were reported as ppm of $\text{NO}_3\text{-N}$ using 3 digits (due to logarithmic scale).
9. Values less than 1 ppm (uncorrected for dilution) were recorded as 1 ppm.

The apparatus used for nitrate analysis is illustrated in Fig. 17.

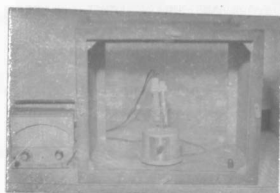


Fig. 17 — Nitrate analysis equipment.

The reference electrode contained a filling solution that was a 1:9 dilution of sat. KCl to water (resaturated with AgCl). The electrode assembly was housed in an electrically grounded copper-screened box to reduce static electricity interferences. A correlation analysis was conducted on nitrate values which were determined both by the electrode measurements and by a phenoldisulfonic-acid analysis conducted by the South Dakota State University soil testing laboratory on 47 soil samples (farmer samples sent to the soil-testing laboratory). Each value reported for either method was an average of duplicate samples. The concentrations ranged from 2.90 to 70.0 ppm. The highly significant correlation coefficient (r) was 0.985.

Approximately 6500 nitrate analyses were conducted and the electrode possessed remarkable stability. During the first 20 to 30 samples each day electrode drift was prevalent with the system requiring calibration after each 3 or 4 samples. After the preliminary few samples, the standardization readings were rarely over 0.1 ppm from the 10 ppm standard solution. Early-day drift was decreased by storing the nitrate electrode in 10 ppm standard solution and capping the reference electrode.

METHODS FOR INDIVIDUAL EXPERIMENTS

A. Laboratory

1. Passage of a freezing front through a saturated sand column

Cores (7.6-cm I.D.) were prepared which contained either moist (10.0%)⁷ or saturated sand. They were placed in a 4.4 C room to equilibrate for 8 hr in the vertical position that they would be frozen. Two (2) ml of saturated (sat.) $\text{Ca}(\text{NO}_3)_2$ solution were applied to the bottom surface of each core. Core freezing from their bottoms began 8 hr after the nitrates were applied. Check cores received the same treatments except they were not frozen. All cores were prepared in triplicate for each of the procedures outlined.

The cores had a freezing plate at one end and a styrofoam cover on the other end. The cold plate was maintained at a measured temperature of -6 ± 0.5 C. In addition, temperatures were recorded at hour intervals for the 0, 6, 12, and 18 cm distances from cold plate.

The unfrozen cores remained at ≈ 4 C and were sampled in 1-cm increments concurrently with the frozen cores (28 hr after nitrate addition). The depth of freezing (assumed to be where the core temperature was 0 C) was calculated at 5-hr intervals (within the 20-hr freezing period) by linear interpolation between two recorded temperatures. Moisture contents were determined for the 1- to 2-cm and 17- to 18-cm depths. An analysis of variance of the nitrate contents was conducted with depth, replication, freezing or no freezing, and

⁷All moisture values are reported as percent of dry weight.

moisture content as the main effects.

2. Freeze-thaw cycles in a saturated Vienna-loam soil

Two (2) ml of sat. $\text{Ca}(\text{NO}_3)_2$ were applied to saturated, undisturbed Vienna-loam soil contained in 7.6-cm I.D. cores. The cores were placed in ECC-B with a styrofoam layer between the two blocks (each containing 6 cores). The cores were positioned so the surface of nitrate application was on the cold plate. Freezing began within an hour after nitrates were applied. Check cores that received all treatments except freezing were maintained at $\approx 4^\circ\text{C}$.

Temperatures were monitored hourly at 1, 5, 10, and 15 cm distances from the cold plate. Each freeze or thaw cycle was timed for 20 hr. The cycles were designated as follows: A = freeze(f), B = freeze-thaw (f-t), C = f-t-f, D = f-t-f-t, and E = f-t-f-t-f. After the 20-hr freeze cycle cores were frozen to at least 15 cm (assuming a 0°C temperature as frozen). After 9 hr of thaw, all core temperatures were greater than 0°C .

Two cores from each block [A(f), C(f), or E(f) where f = frozen] along with 2 check cores [A(u), C(u), or E(u) where u = unfrozen] for each block were removed after the completion of cycles A, C, and E. Dummy cores of similar materials were placed in the void spots in ECC-B left when cores were sampled. The cores were sampled by 1-cm increments and analyzed for nitrates. Nitrate contents of the two replications were averaged and then the averages of check treatments were subtracted from their analogous frozen treatment. The differences found in the different freeze-thaw cycles and the different sample

depths were analyzed statistically. The analysis of variance used depth, soil freezing time, and position as main effects.

Another procedure was used for the cores contained in the top block to analyze the direct effects of freezing and thawing. Use of this method assumed that the thawing cycle could be reduced to a "zero-time thaw interval". This procedure estimated the nitrate contents at the different depths that were caused only by movement during the freeze-thaw cycles. The nitrate contents with depth in soil cores that were not frozen were used for correction values. This procedure did not correct for nitrate movement caused by thermal and moisture gradients which were present in a thawing core. The estimated nitrate contents with depth after successive cycles (A^1 , C^1 , or E^1 where 1 = estimated values for each given cycle) were obtained in the following manner: $A^1(f)$ = nitrate contents with depth in $A(f)$ (no correction needed), $C^1(f)$ = corrected nitrate contents with depth for $C(f)$ [corrected by subtracting the nitrate contents with depth in $A(u)$ from nitrate contents in $C(f)$], and $E^1(f)$ = corrected nitrate contents with depth in $E(f)$ (corrected by subtracting the nitrate contents with depth after 40 hr in unfrozen cores [determined by linear extrapolation between values obtained for $A(u)$ and $C(u)$] from contents of cores from $E(f)$).

3. Nitrate distribution after a freeze-thaw cycle with nitrates applied to the end that was not frozen

Undisturbed Vienna-loam soil cores at either 0- or 0.34-atm of moisture tension received an application of 2 ml of sat. $\text{Ca}(\text{NO}_3)_2$

solution. The nitrate application end of the cores was against the aluminum heat-flux plate (warm end). The saturated cores were frozen downward toward the core's warm end in the top block and the unsaturated cores were frozen upward toward the core's warm end in the bottom block of ECC-B.

Freezing began within 5 hr after the application of nitrates. Temperatures were monitored at 0, 6, 12, and 18 cm distances from the cold plate. Plate temperatures of ≈ -11 and $\approx +11$ C were maintained for 118 hr at the two ends of each core. After this time the frozen soil zone was approximately 8-cm thick (both observed when sampled and calculated by assuming linear gradients between two measured temperature points).

From each of the two blocks, two cores were sampled frozen for nitrate analyses. In addition, two cores were allowed to thaw at ≈ 4 C for 23 hr and were then sampled. Nitrates were analyzed in duplicate for each 1-cm increment of the cores. The 0- to 1-cm increment nitrate value was not included with the other values in the analysis of variance because the distribution with depth between freezing treatments was the factor being evaluated.

4. Nitrate movement in a sand or clay-sand mixture at -5 C

Either 450 g of montmorillonite or 450 g of kaolinite clay was dispersed in 6 l of 6×10^{-3} N sodium hexametaphosphate solution by mechanical shaking. The suspensions were placed at room temperature (≈ 28 C) to allow particles greater than 2μ to settle past 10 cm (Jackson, 1956). The upper 10 cm of each suspension was siphoned off

and divided into 2 portions. Each portion was brought to either a 2 N calcium- or sodium-acetate concentration. One (1) g/l of NaCl or CaCl_2 was added to the suspensions containing sodium- or calcium-acetate, respectively. The suspensions were vacuum filtered through Buchner funnels containing Whatman #50 filter paper. The first washing was with a 50%-methanol aqueous solution and subsequent washings were with a 95%-methanol aqueous solution. Washing continued until a negative chloride test (using AgNO_3) was observed on the filtrate. The clays were kept moist at all times while being filtered to avoid cracking. The washed clays were air dried. The moisture contents of the air-dried clays and of the sands were determined (105 C). Appropriate amounts of air-dried clay and sand (60 to 140 mesh) were combined to prepare mixtures of 20% clay and 80% sand. The mixtures were brought to a 20% moisture content and ground using a mortar and pestle to assure thorough mixing and to coat all sand particles with clay. Some of the cores were saturated by capillary rise. Only the calcium-saturated mixtures would conduct enough water to cause saturation. The sand cores were prepared by filling tubes with dry sand and then they were saturated with water. All cores were prepared in triplicate for each of the procedures outlined.

The cores were placed in styrofoam blocks and allowed to freeze from both ends for 24 hr at approximately -10 C in a walk-in freezer. Two drops of 166 g/l $\text{Ca}(\text{NO}_3)_2$ or 171 g/l NaNO_3 solution were applied to one end of each core. Two cores of each clay mixture received no nitrate application and were used to check for variable electrode

junction potentials. The sand cores received a $\text{Ca}(\text{NO}_3)_2$ addition and no check sand-cores were prepared because variable junction potentials were previously found not to develop in this sand.

The cores were placed in ECC-A with a temperature controlled plate (using one power source) at either end of the cores. Temperatures were monitored during the 3-week duration at both core-plate interfaces. They ranged from -6.1 to -3.3 C with the majority between -6.1 to -4.4 C.

Sampling the 10-cm-long cores was accomplished by slicing through the slits between the 0.8-cm lengths of tube. The samples were allowed to air dry and nitrate analyses were conducted using 1 g of sample with 10 ml of water-extracting solution.

An analysis of variance with depth, replication, and soil as the main effects was conducted. Another analysis was conducted using values calculated for each core by taking the ratio of the nitrates found in the 1- to 10-cm depth to total nitrates in the column.

5. Nitrate movement in frozen saturated soils that were subjected to a temperature gradient

Kyle-clay, Vienna-loam, and Egeland-sandy-loam disturbed soils were packed into 2.5-cm I.D. (5-cm long) cores, saturated, and placed in drill holes in a styrofoam sheet (Fig. 6). The cores, insulated except on their ends, were subjected to a temperature of ≈ -10 C for 24 hr in a walk-in freezer. One (1) drop of sat. $\text{Ca}(\text{NO}_3)_2$ was applied to one end of each core. The block of cores was placed in ECC-A with the cold and warm ends held at -3.3 and -0.5 C, respectively, for 164 hr. Nitrates were applied either on the warmer or cooler core end. Check cores for each treatment (no nitrate application) were also subjected

to the similar temperature differential. All cores were prepared in duplicate for each of the procedures outlined. Temperatures were monitored at hour intervals at both plate-core interfaces and at the middle of the column. During the 164-hr period, temperatures of slightly greater than 0 C were measured for a consecutive 6-hr period.

The cores were sampled by cm increments and duplicate samples were analyzed for nitrates for each depth. The reported values were the differences between the treatment and check cores. If the difference was less than or equal to zero the nitrate content was recorded as 0 ppm. An analysis of variance of these differences was conducted using position, replication, depth, and type of soil as main effects.

6. Others

The uniformity of the density of a sand column, which was compacted using 1810 kg of pressure, was analyzed using values obtained from both gamma-ray attenuation and gravimetric moisture determinations. Various size-fractions of sand with different moisture contents in 7.6-cm I.D. polyethylene cores were placed in a gamma-ray beam to determine attenuation at each cm-depth increment. Moisture contents were calculated assuming constant density with depth for each core. The cores were then sampled at cm-depth increments and the moisture content was determined gravimetrically. The moisture contents from each determination for each depth within each core were correlated.

Other nitrate-movement experiments were designed, implemented, and most were analyzed. These included: nitrate movement caused by passage of a freezing front through columns with various initial nitrate distributions, nitrate movement in columns which had their two ends at

different temperatures and were initially uniform in nitrate contents with depth, movement of nitrate from its application surface when each of the two ends of the core were maintained at different subfreezing temperatures, and nitrate movement during multifreezing and thawing cycles in various soils at specified moisture contents. Both disturbed and undisturbed soil cores were used in either ECC-A or ECC-B.

B. Field

1. Year 1 — Nitrate distribution after fall or winter application

The soil moisture content in the fall averaged 24.6% for the 0- to 17-cm depth. The "before freeze" nitrate was applied (570 kg/hectare of solid $\text{KNO}_3\text{-N}$) October 16 with the "after freeze" treatment applied January 15. Three replications of each treatment were used.

Plots and cores were sampled April 1. At the time of sampling (the warmest day to date that spring) solid frost began at an ≈ 8 -cm depth. Ice crystals were present in the 0- to 8-cm layer. Nitrate contents were determined for each cm increment (totaling 17) and moisture contents for alternate depths. An analysis of variance was conducted using depth, replication, time of application, and core or no core treatments as main effects.

2. Year 2 — Nitrate distribution after fall or winter application

Egeland-sandy-loam, Vienna-loam, and Kyle-clay disturbed soils were placed in 7.6-cm I.D. cores. They were brought to moisture tensions of either 0, 0.34, or 1.02 atm. Nitrates were applied as 2 ml of sat. $\text{Ca}(\text{NO}_3)_2$. Two separate experiments were performed with the disturbed core samples (a,b). In addition, one experiment with undisturbed field soils was performed (c).

- a. All three soils at each moisture level were placed in the field either before or after freezing with nitrates applied to the top surface. All cores were prepared in duplicate.
- b. The Egeland-sandy-loam and Vienna-loam soils at either 0.34 or 1.02 atm of moisture tension were used for diffusion columns. Nitrates were applied either on the top or bottom of the cores which were placed in the field either before or after freezing. All cores were placed in styrofoam blocks with the bottoms of each core in thermal contact with the underlying soil. All cores were prepared in duplicate.
- c. Nitrates were applied to undisturbed Vienna-loam soil either before or after freezing on either uncovered plots or plots covered with polyethylene sheeting. Nitrates were applied as powdered $\text{Ca}(\text{NO}_3)_2$ at 570 kg/hectare.

For the experiments (a, b, and c) the before freezing treatments were applied October 31, 1971, with the after freezing treatments applied January 8, 1972. Sampling occurred on March 5, 1972. Temperatures were monitored on the warmest days for 1, 5, 10, 15, 20, 30, 50, 70, 100, and 160 cm depths. Soil moisture contents for the surrounding area were determined for 10-cm increments to a depth of 70 cm on the dates listed above. Nitrates were analyzed for each 3-cm increment of depth. The starting base for the first depth was the end on which nitrates were applied (whether bottom or top). Analyses of variances of nitrate values for (a) and (b) were conducted using appropriate treatments as main effects.

RESULTS AND DISCUSSION

Passage of a freezing front through either saturated or unsaturated sand columns caused a net movement of nitrate ions in the direction of freezing greater than could be accounted for by diffusion. Figure 18 illustrates the distribution of nitrates in sand columns under the conditions described by Experiment A-part 1 (Exp. A-1).

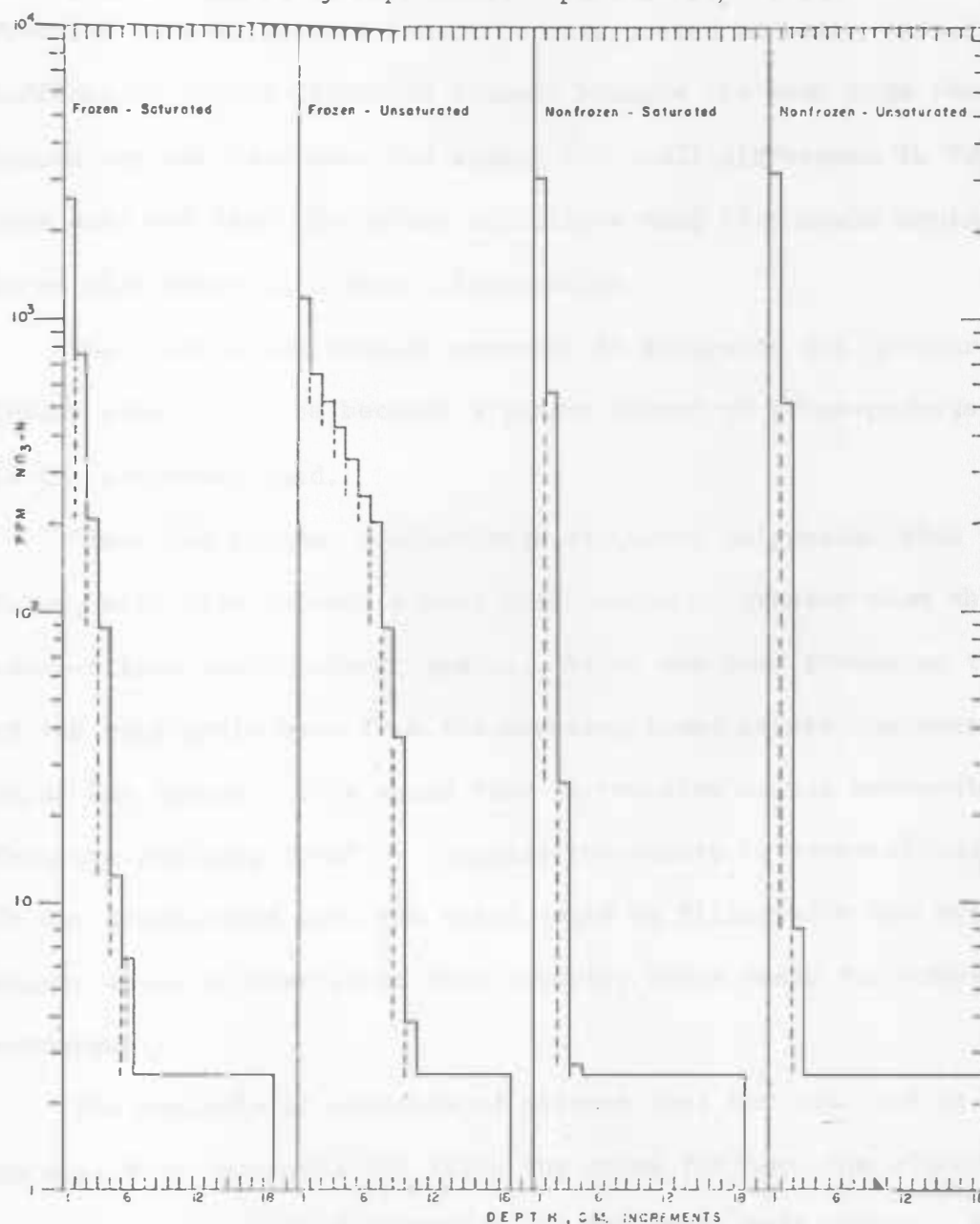


Fig. 18 — Distribution of nitrate ions in either frozen or unfrozen sand columns. $\bar{S}X = 5.0$

Note the greatest movement occurred in unsaturated columns which were frozen. The analysis of variance and means are presented in Appendix A (App. A).

The depth and rate of freezing are reported in App. A-d. The unsaturated sand froze at a faster rate than the saturated sand. The freezing rate difference cannot be interpreted as being caused by differences in the diffusion columns because the heat flux from each column may not have been the same. The small difference in freezing rate does not lead the author to believe that this could explain the large difference in nitrate distribution.

The differences between movement in saturated and unsaturated frozen sands could be because a larger number of brine-pockets formed in the saturated sand.

Since the thermal conductivity of quartz is greater than that for water, heat flow through a sand grain would be greater than through water-filled voids between grains. Water may have frozen on the side of the sand grain away from the freezing front before the water in the voids was frozen. This would tend to restrict solute movement away from the freezing front by trapping the solute in water-filled voids. In the unsaturated sand the voids would be filled with air and the solute would be restricted from entering these areas for subsequent entrapment.

The analysis of variance of nitrate data for Exp. A-2 is presented in App. B-a. Appendix B-b lists the means for both the block (freezing direction)- by-depth interaction and the depth main effect. The block-by-depth means appear to be different mainly in the 0- to 1-cm depth

increment and therefore are difficult to interpret. Except for the surface increment, values tend to be negative in the upper part of the core and positive in the lower part. The negative trend probably was caused by diffusion inhibition in the frozen cores next to the surface where nitrate was applied. Below the 6- to 7-cm depth, all values were positive. This nonrandom distribution suggests that the nitrate contents within frozen cores were greater below the surface zone of diffusion inhibition than within cores receiving no freezing treatment. Nitrates may have been relocated when the freezing front passed through the core.

Data presented in Table 1 yields evidence that movement of nitrates occurred with each freeze-thaw cycle if the data were corrected to zero diffusion time.

Table 1 — Nitrate means (ppm $\text{NO}_3\text{-N}$) for Exp. A-2 involving multifreezing of a saturated Vienna-loam soil.

Depth Increment	Treatment				
	$A^1(f)$	$C^1(f)$	$E^1(f)$	$A^1(f)+C^1(f)+E^1(f)$	$C(u)$
1	nr	nr	nr	nr	nr
2	187	333	425	945	1250
3	41.3	69.9	307	418	281
4	27.5	19.0	24.6	71.1	54.1
5	6.66	3.19	18.5	28.3	7.80
6	6.02	4.46	3.71	14.2	4.28

where nr = not reported, depth-increment 1 = 0-1 cm . . . 6 = 5-6 cm, $A^1(f)$; $C^1(f)$; $E^1(f)$ = corrected nitrate distribution due to first, second, and third freeze-thaw cycles, respectively (corrected to zero time diffusion), $A^1(f)+C^1(f)+E^1(f)$ = the total corrected nitrate distribution after three freeze-thaw cycles, and $C(u)$ = distribution in unfrozen soil after the same time interval as $[A^1(f)+C^1(f)+E^1(f)]$.

The corrected data are not quantitative values but are semi-quantitative estimates of nitrate distribution after consecutive freeze-thaw cycles with zero thaw time.

Movement of nitrate associated with unidirectional freezing through the sand and Vienna-loam soils probably involved many processes. Salt rejection from the ice into the freezing water with concurrent diffusion of the concentrated salts was a mechanism for movement away from the freezing front. The formation of brine pockets which have lower freezing points would tend to allow the freezing front to move more rapidly than the nitrates. The brine pockets subsequently may have been subjected to gravity flow through the column. Movement of water both to and from the freezing front may have carried soluble salts. Salts may also have migrated slowly through unfrozen films in the frozen materials but the prior two experiments were probably not conducted long enough for this to be important.

The analysis of variance for Exp. A-3 is presented in App. C. The nitrate means involved in the highly significant SFD (soil-by-freezing-by-depth), FD, SD, and D interactions and main effects can be readily observed in Table 2.

Table 2 — Nitrate distribution (ppm $\text{NO}_3\text{-N}$) with depth after either a freeze or freeze-thaw cycle in Vienna-loam soil either at 0 or 0.34 atm of moisture tension with nitrates applied to the warm end of the column.

Column	(a)	(b)	a-b	(c)	(d)	c-d
Freezing treatment	Frozen	Frozen & thawed	Diff.	Frozen	Frozen & thawed	Diff.
Water tension	0.34 atm	0.34 atm		0 atm	0 atm	
Depth increment						
1	nr	nr	nr	nr	nr	nr
2	882	1370	-488	927	1470	-543
3	251	411	-160	445	831	-386
4	68.4	90.0	-21.6	169	361	-192
5	21.4	28.7	-7.3	61.4	136	-74.6
6	9.95	11.7	-1.75	30.0	53.4	-23.4
7	8.18	6.25	1.93	16.1	20.1	-4.00
8	9.21	6.41	2.80	13.1	11.1	2.00
9	9.67	5.62	4.05	12.2	9.53	2.67
10	12.3	6.58	5.72	15.2	10.0	5.20
11	14.6	8.04	6.56	15.5	11.3	4.20
12	16.2	10.5	5.70	16.1	11.9	4.80
13	13.8	10.9	2.90	15.7	13.2	2.50
14	17.9	11.4	6.50	14.3	13.8	0.50
15	14.4	8.53	5.87	16.4	14.1	2.30
16	13.1	7.07	4.57	16.0	13.6	2.40
17	10.4	6.07	4.33	17.8	10.9	6.90
18	16.7	11.3	5.40	23.6	9.26	14.3

where nr = not reported, depth-increment 1 = 0-1 cm . . . 18 = 17-18 cm
frozen = cores sampled while frozen, frozen and thawed = cores sampled when thawed, and diff. = difference in concentration between the two indicated columns.

For the Vienna-loam soil at both moisture levels, the concentrations beyond the 6- to 7-cm depth were less for the thawed than for the

frozen cores. Water may have moved to the cold end during freezing and may have been redistributed during thawing. With the redistribution of water there appears to have been an accumulation of nitrates toward the warm end where the nitrates were applied. A mechanism for nitrate movement therefore was created by water migration during freezing and thawing.

The nitrate concentration means for depth for various classes of soil materials at given moisture levels for Exp. A-4 are presented in Fig. 19 (refer to App. D-a for the analysis of variance).

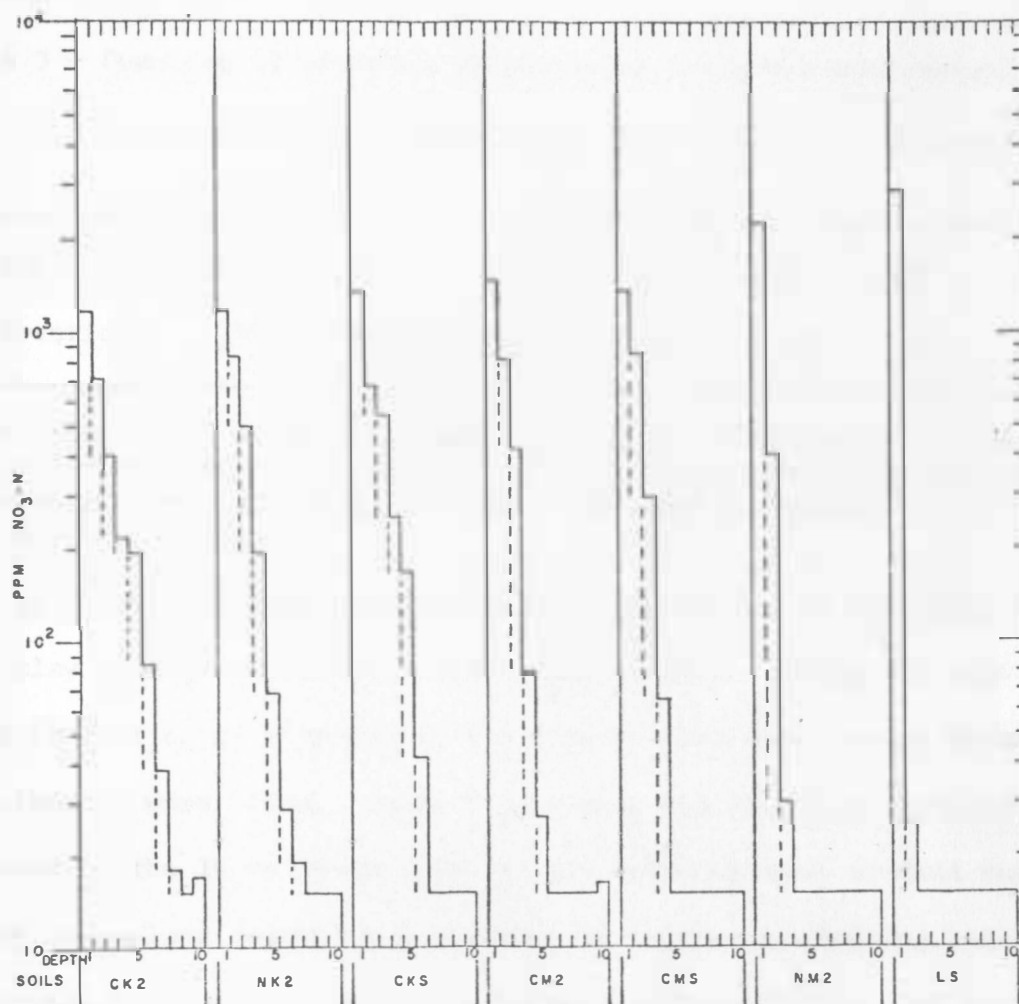


Fig. 19 — Nitrate distribution in sand and clay-sand mixtures used in Exp. A-4 when column temperatures were held at ≈ -5 C for a 3-week duration.

where depth 1 = 0-1 cm . . . 10 = 9-10 cm, C = calcium saturated, N = sodium saturated, K = kaolinite, M = montmorillonite, L = sand, 2 = moisture level at 20%, and S = moisture level at saturation. $\bar{S}_x = 18.6$.

The columns in Fig. 19 and Table 3 are ranked from left to right in the order of the decreasing nitrate content found in the 1- to 10-cm depth divided by the amount in the 10-cm long core (refer to App. D-b for the analysis of variance). This fraction measured nitrate

movement from the 0- to 1-cm depth.

Table 3 — Fraction of nitrates in the 1- to 10-cm depth to total in the core for sand and clay-sand mixtures maintained at -5 C for 3 weeks.

Soil	CK2	NK2	CKS	CM2	CMS	NM2	LS
Fractions	0.595	0.592	0.564	0.492	0.468	0.191	0.036

where soil = same notation as used in Fig. 19 and fractions = fraction of the nitrate measured in the 1- to 10-cm increment to the nitrate measured in the 0- to 10-cm increment (average of 3 reps).
 $\bar{S}X = 0.035$

It is evident from data presented in both Fig. 19 and Table 3 that clay types, saturating cations, and moisture levels all affected the distribution of nitrates in the columns that were frozen before the nitrates were added. Table 3 indicates the fraction (nitrate measured in the 1- to 10-cm depth to the total nitrate content measured in the 10-cm-long column) was greater for columns containing kaolinite clays than for columns containing montmorillonite clays. For the columns at a 20% moisture level, the fraction appeared to be dependent upon saturating cation for the montmorillonite columns but not for the kaolinite columns. Both calcium-saturated-clay types had a smaller fraction in the saturated in comparison to the unsaturated columns. Very little movement occurred in the saturated sand.

The difference in movement between the saturated and unsaturated soils was probably due to a reduction in continuous films in the saturated soils. As water froze and expanded in the pores soil particles were pushed apart which resulted in decreased numbers of continuous liquid like films available for nitrate movement. As previously indicated,

different homoionic-clays possess similar thicknesses of liquid-like water at approximately -5 C. Also the $d(001)$ for the different ionic saturations are similar at this temperature. Therefore, differences in nitrate movement for either sodium- or calcium-saturated kaolinite and montmorillonite were probably due to nitrate-to-clay-surface interactions. When the diffuse double-layer is thicker (i.e. sodium compared to calcium) restriction of nitrate movement could be caused by negative adsorption. This effect would cause restriction of nitrate movement by small pores and thin liquid films and could produce the observed results for the sodium- versus calcium-saturated montmorillonite soil. Evidently, effects of the diffuse double layer did not alter nitrate movement in the calcium- or sodium-saturated kaolinite system. Movement in the sand columns was small probably because continuous unfrozen water films were nearly absent.

Table 4 illustrates the nitrate content means for the position-by-depth-by-soil (PDS) interaction for Exp. A-5.

Table 4 — Nitrate content means (ppm $\text{NO}_3\text{-N}$) for the PDS interaction in
Exp. A-5.

Soil	Kyle Clay		Vienna Loam		Egeland Sandy Loam	
Position	Warm	Cold	Warm	Cold	Warm	Cold
Depth						
1	453	698	516	688	588	638
2	416	238	235	185	298	340
3	158	60.8	48.0	5.97	80	78.0
4	19.5	3.66	15.1	0	15.9	18.5
5	0.81	5.17	3.95	0	13.6	13.2

where depth 1 = 0-1 cm . . . 6 = 5-6 cm and position = nitrates applied
either to warm or cold end of the columns.
 $S\bar{X} = 21.5$

Movement of nitrates from the application surface was evident for all soils described in Exp. A-5. Movement from the warm (-0.5°C) surface was greater than movement from the cold surface (-3.3°C) except for the Egeland sandy loam. Many factors could have been involved. The Soret effect, nitrate movement with mass flow of water to the cold surface, liquid-like films with different thicknesses as diffusion paths, formation of ice lenses, and negative absorption qualities of various soils could not be distinguished in the experiment. The small difference in distributions for the Egeland-sandy-loam soil could have been due to its insensitivity to any of these factors. The data illustrate that nitrate movement in frozen soils did occur

for the described conditions.

Results obtained from the procedures described in Exp. A-6 were variable in most cases, and offered little interpretable information. Correlation coefficients (r) ranging from 0.25 to 0.98 were calculated for the comparisons of moisture contents determined by either gamma-ray attenuation procedures or gravimetric methods. For the grade 0 silica-sand, which was used in the nitrate-movement studies, (r) was 0.83 and 0.75 for two different cores each at an average 10% moisture content. These values indicate that up to 69% of the variation in measured gamma-ray values could be accounted for with moisture content changes. Therefore, 31% of the variation was due to factors other than moisture content which could have included density changes.

Results from the nitrate-movement procedures described in Exp. A-6 are not presented in detail. In many cases, the experimental variability was so large that the main effects or interactions were not significant. The variability appeared to be reduced when disturbed rather than undisturbed diffusion columns were used. Equipment malfunctions caused some experimental durations to be too short for detectable nitrate movement. Compaction of undisturbed soils in cores during multifreezing and thawing cycles caused nitrate movement by movement of the soil from one depth to another. In most cases, nitrate moved during freezing or in frozen systems but no statistically significant differences were found between the frozen and unfrozen systems.

The analysis of variance for the first-year's field experiment (Exp. B-1) is presented in App. F. The depth-by-nitrate application (DN) was of major interest and the nitrate means are plotted in Fig. 20.

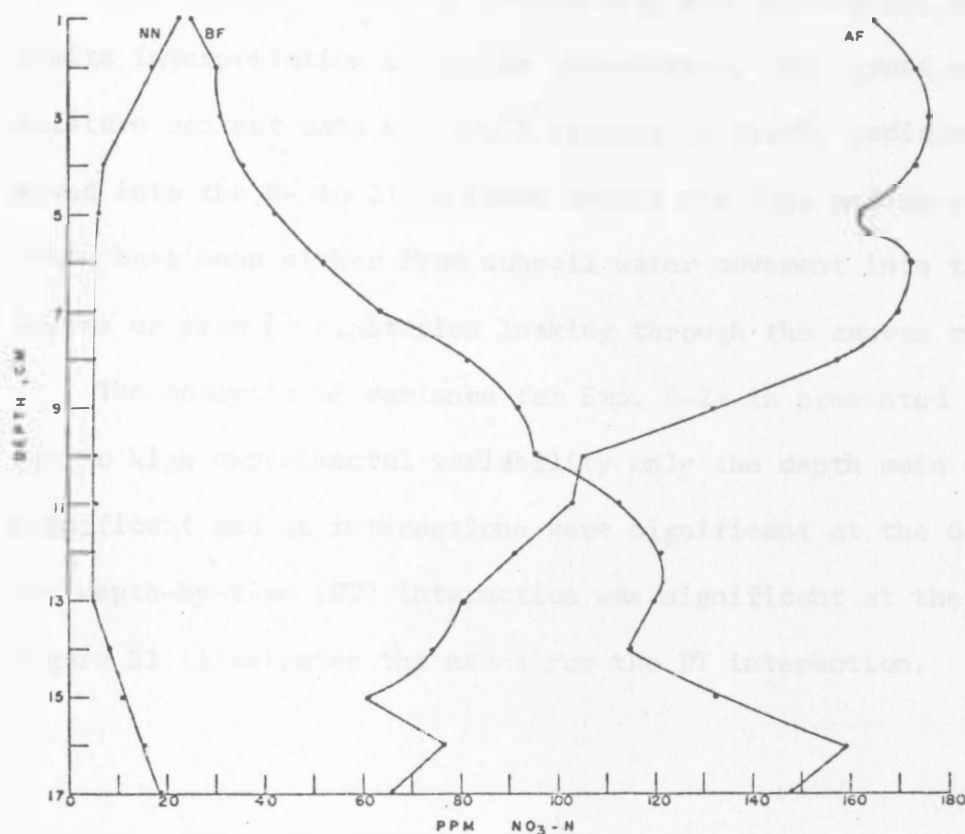


Fig. 20 — The DN interaction means for Exp. B-1: where NN = no nitrates applied, BF = nitrates applied before freeze, and AF = nitrates applied after freeze.

$$\bar{Sx} = 21.8$$

Figure 20 reveals that nitrates did move under the conditions described in Exp. B-1. However, the experiment was difficult to interpret because no temperature data were taken to confirm that the system remained frozen between the after-freeze-treatment application and the sampling time. The DNC (DN-by-core) interaction was significant which again limits interpretation of the DN interaction. The grand mean of the moisture content data was 39.1% (initially 24.6%) indicating that water moved into the 0- to 17-cm layer during the fall and/or winter. This could have been either from subsoil water movement into the surface layers or from precipitation leaking through the canvas covering.

The analysis of variance for Exp. B-2a is presented in App. G. Due to high experimental variability only the depth main effect was significant and no interactions were significant at the 0.05 level. The depth-by-time (DT) interaction was significant at the 0.1 level. Figure 21 illustrates the means for the DT interaction.

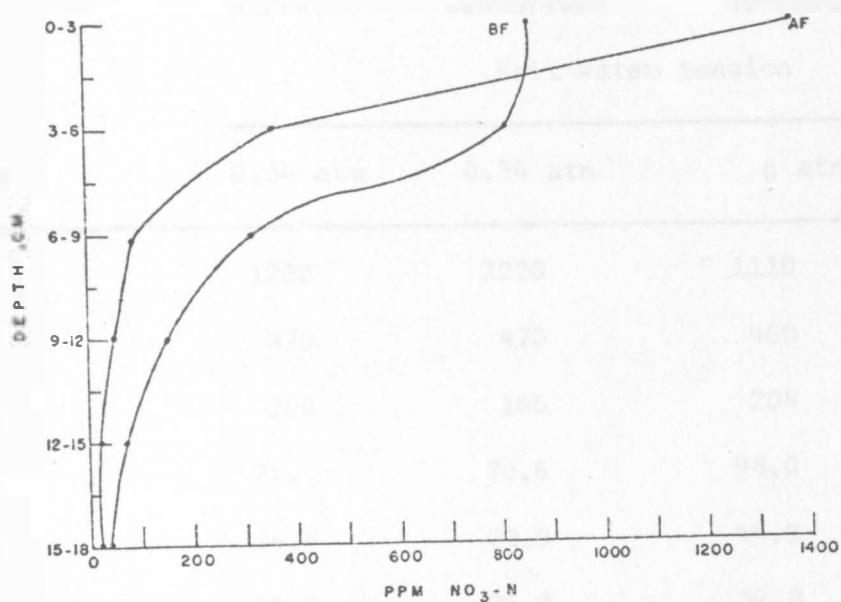


Fig. 21 — Means for the DT interaction in Exp. B-2a: where BF = application before freeze and AF = application after freeze.

A greater nitrate movement occurred when the time of application was before rather than after freezing. The experiment confirms movement occurred even when the soils were frozen. At the times measured, no soil temperatures were greater than 0 C between the after-freeze-treatment application and the sampling date.

The analysis of variance for Exp. B-2b is presented in App. G-c. The interactions of major interest were those containing depth terms. The depth-by-position-by-moisture level (DPM) and depth-by-time-by-soils (DTS) were significant.

Table 5 -- Nitrate means (ppm $\text{NO}_3\text{-N}$) for the DPM interaction in Exp. B-2b.

Depth	Nitrate Application Surface			
	Surface	Subsurface	Surface	Subsurface
	Soil water tension			
	0.34 atm	0.34 atm	0 atm	0 atm
1	1220	1220	1110	1110
2	470	470	460	446
3	166	166	204	190
4	71.1	70.6	98.0	84.2
5	34.4	33.9	44.9	31.1
6	26.7	26.2	39.8	26.1
fraction	0.386	0.386	0.432	0.414

where depth 1 = 0-3 cm . . . 6 = 15-18 cm and fraction = the sum of the values between 3 and 18 cm to the total in the 0- to 18-cm core.
 $\bar{Sx} = 17.2$

The greater fractions which occurred for the saturated than for the unsaturated soils (Table 5) probably resulted from greater nitrate movement from the 0- to 3-cm depth. The nitrate contents with depth tended to be greater for the surface-applied saturated treatment than for the subsurface-applied saturated treatment but the same trend did not occur for the unsaturated treatments. Due to a thick snow cover the surface temperature gradients were small. Therefore, significant water movement upwards within the cores would not be expected. The nitrate

values reported in Table 5 do not distinguish between the before- or after-freeze-nitrate-application treatment. The DPMT interaction was not significant.

The data in Table 6 suggest that a larger difference in nitrate content for depth 1 between the before and after freeze was present for Vienna loam than the Egeland sandy loam. This may suggest that the frozen soils in comparison to the unfrozen soils had a larger proportion of the ions moved in the finer textured Vienna-loam soil during the frozen period.

Table 6 — Nitrate means (ppm $\text{NO}_3\text{-N}$) for the DTS interaction in Exp. B-2b.

Depths	Vienna loam			Egeland sandy loam		
	NO_3 application			NO_3 application		
	before freeze	after freeze	diff.	before freeze	after freeze	diff.
	(a)	(b)	a-b	(c)	(d)	c-d
1	901	1470	-569	911	1370	-459
2	626	338	288	518	364	154
3	277	127	150	269	53.1	216
4	148	55.2	92.8	102	18.6	83.4
5	59.1	43.0	16.1	22.5	8.80	13.7
6	47.2	53.1	-5.9	11.8	6.71	5.09

where 1 = 0-3 cm . . . 6 = 15-18 cm.,

$\overline{SX} = 17.5$

Table 7 illustrates nitrate distributions with depth for Exp. B-2c. With the sampling procedure used interpretation of the various treatments were difficult so the covered and noncovered treatments were summed to

obtain the reported means.

Table 7 — Nitrate (ppm $\text{NO}_3\text{-N}$) distribution for Exp. B-2c.

Depth	Nitrate application treatments		
	Nitrates applied before freeze	Nitrates applied after freeze	No nitrates applied
1	460	359	52.1
2	309	84.9	48.2
3	89.0	49.1	39.1
4	53.5	53.4	38.7
5	39.4	41.5	38.3
6	34.6	28.6	33.2
7	30.9	23.5	31.8

where 1 = 0-10 cm, 2 = 10-20 cm . . . 7 = 60-70 cm.

Even though each value reported was the composite of five subsamples and was summed over two replications (after combining the covered and non-covered treatment) the total recovery of the applied nitrates for the before- or after-freezing treatment was dissimilar. This leads the author to believe that a representative sample was not obtained. However, it appears that nitrate movement could have occurred to depths of 30 to 40 cm in both before- and after-freeze applications. The nitrate content of the snow at 0 to 2 cm from the ground surface over the uncovered plots averaged 2.7 ppm $\text{NO}_3\text{-N}$.

CONCLUSIONS

Nitrate movement in freezing or frozen soils could involve the following mechanisms: salt rejection from the ice in the freezing soil solution, diffusive flow due to salt concentration gradients, movement with mass flow of water, either diffusive or gravity migration of brine pockets, and redistribution due to thermally induced ion-activity gradients (Soret effect). Many movement mechanisms require continuous, liquid-like moisture films to be present. Most of the mechanisms are influenced by various soil properties.

Nitrate movement in the direction of freezing in saturated or unsaturated sand columns was greater than movement by diffusion in similar but unfrozen sand columns. Salt rejection from the ice in the freezing soil solution probably caused this movement. The movement was greater for unsaturated than for saturated sand possibly because more brine pockets were formed and were trapped in the ice in saturated soils. Cores of saturated Vienna loam, that were frozen and thawed successively, had nitrate distributions after each freeze-thaw cycle which could have been caused by nitrate movement away from the freezing front in each cycle.

Transport of nitrates by the mass flow of water as the soil froze and thawed was a movement mechanism. In an unidirectionally frozen and thawed column, nitrates moved toward the warm end, with the highest nitrate concentration, during the thaw cycle. This was probably because water moved toward the cold end during freezing and away during thawing.

Nitrate movement away from an application surface in "frozen" (-5 C) clay-sand mixtures was influenced by the clay type, the clay's exchangeable cations, and the moisture content. Negative adsorption of nitrate by clay surfaces and the interruption of liquid-film continuity by thin ice lenses probably were the major factors controlling nitrate movement. In comparison to the sand-clay mixtures, very little movement occurred in saturated sand columns due to the lack of continuous, unfrozen liquid-like films.

Nitrates, applied to either the cold (-3.3 C) or warm (-0.5 C) end of saturated columns of Kyle clay, Vienna loam, or Egeland sandy loam, moved from the application surface where the nitrate concentration was high. Larger concentrations were measured in the application end when the application was on the cold end instead of the warm end for both Kyle clay and Vienna loam but not for the Egeland sandy loam. Movement mechanisms involved probably were diffusion due to concentration or thermal gradients, brine-pocket migration, and movement with mass flow of water. Temperature differences between the ends of the frozen core caused the liquid films to be thinner in the cold end than in the warm end. Therefore, ion movement away from the cold end was less because the liquid-like films were thinner. In addition, liquid-water movement could have transported nitrates back to the cold end. Field studies revealed that either fall or winter surface-applied nitrate migrated downward away from the surface to depths of about 30 cm.

Thus, nitrates moved during soil freezing and in frozen soils. The movement was dependent upon the temperature and temperature gradients in the soil system and upon various physical and chemical

properties of the soil which affected the nitrate movement mechanisms.

BIBLIOGRAPHY

- Anderson, D. M. 1966. Phase composition of frozen montmorillonite-water mixtures from heat capacity measurements. Soil Science Society of America Proceedings 30:670-675.
- Anderson, D. M. 1968. Phase boundary water in frozen soils. Paper presented at Symposium: Freezing and Thawing Phenomena in Soils, Soil Science Society of America Annual Meeting, New Orleans, Louisiana. Also abstract found in: Agronomy Abstracts, 1968 Annual Meetings of the American Society of Agronomy, Madison, Wisconsin.
- Anderson, D. M. and P. Hoekstra. 1965. Migration of interlamellar water during freezing and thawing of Wyoming bentonite. Soil Science Society of America Proceedings 29:498-504.
- Anderson, D. M. and A. R. Tice. 1971. Low-temperature phases of interfacial water in clay-water systems. Soil Science Society of America Proceedings 35:47-54.
- Babcock, K. L. 1963. Theory of chemical properties of soil colloidal systems at equilibrium. Hilgardia 34:417-542.
- Bouyoucos, G. J. 1917. Measurement of the inactive or unfree moisture in the soil by means of the dilatometer method. Journal Agricultural Research 8:195-217.
- Bremner, J. M., L. G. Bundy, and A. S. Agarwal. 1968. Use of a selective ion electrode for determination of nitrate in soils. Analytical Letters 1:837-844.
- Campbell, C. A., W. S. Ferguson, and F. G. Warder. 1970. Winter changes in soil nitrate and exchangeable ammonium. Canadian Journal of Soil Science 50:151-162.
- Cary, J. W. 1966. Soil moisture transport due to thermal gradients: Practical Aspects. Soil Science Society of America Proceedings 30:428-433.
- Cary, J. W. and H. F. Mayland. 1972. Salt and water movement in unsaturated frozen soil. Submitted to Soil Science Society of America Proceedings. Also abstract found in: Western Society of Soil Science Abstracts, June 16-18, 1971, at University of Wyoming, Laramie.
- Corte, A. E. 1962. Vertical migration of particles in front of a moving freezing plane. Journal of Geophysical Research 67:1085-1090.

- Corte, A. E. 1963. Particle sorting by repeated freezing and thawing. *Science* 142:499-501.
- Dahnke, W. C. 1971. Use of the nitrate specific ion electrode in soil testing. Personal communication.
- Dirksen, C. and R. D. Miller. 1966. Closed-system freezing of unsaturated soil. *Soil Science Society of America Proceedings* 30:168-173.
- Edwards, D. G., A. M. Posner, and J. P. Quirk. 1965. Repulsion of chloride ions by negatively charged clay surfaces. Part I. — Monovalent cation fithian illites, and Part 3. — Di- tri-valent cation clays. *Transactions of the Faraday Society* 61:2808-2823.
- Fay, A. H. 1920. A glossary of the mining and mineral industry. U.S. Bureau of Mines Bulletin No. 95. 754 p.
- Ferguson, H., P. L. Brown, and D. D. Dickey. 1964. Water movement and loss under frozen soil conditions. *Soil Science Society of America Proceedings* 28:700-703.
- Gardner, W. R. 1965. Movement of nitrogen in soil. In W. V. Bartholomew and F. E. Clark (ed.) *Soil Nitrogen*. American Society of Agronomy Monograph 10, Madison, Wisconsin p. 555-572.
- Groot de, S. R. and P. Mazur. 1962. *Non-equilibrium thermodynamics*. Interscience Publishers Inc., New York. 510 p.
- Hemwall, J. B. and P. F. Low. 1955. The hydrostatic repulsive force in clay swelling. *Soil Science* 82:135-145.
- Hoekstra, P. 1965. Conductance of frozen bentonite suspensions. *Soil Science Society of America Proceedings* 29:519-522.
- Hoekstra, P. 1966. Moisture movement in soils under temperature gradients with the cold-side temperature below freezing. *Water Resources Research* 2:241-250.
- Hoekstra, P. 1969. Water movement and freezing pressure. *Soil Science Society of America Proceedings* 33:512-518.
- Hoekstra, P. and E. Chamberlain. 1964. Electro-osmosis in frozen soil. *Nature* 203:1406-1407.
- Hoekstra, P. and R. D. Miller. 1967. On the mobility of water molecules in the transition layer between ice and a solid surface. *Journal of Colloid and Interface Science* 25:166-173.
- Hoekstra, P., T. E. Osterkamp, and W. F. Weeks. 1965. The migration of liquid inclusions in single ice crystals. *Journal of*

Geophysical Research 70:5035-5041.

- Jackson, M. L. 1956. Soil chemical analysis - advanced course. University of Wisconsin College of Agriculture, Madison, Wisconsin. 991 p.
- Jellinek, H. H. G. 1967. Liquid-like (transition) layer on ice. Journal of Colloid and Interface Science 25:192-205.
- Kemper, W. D. 1960. Water and ion movement in thin films as influenced by electrostatic charge and diffuse layer of cations associated with clay mineral surfaces. Soil Science Society of America Proceedings 24:10-16.
- Kingery, W. D. and W. H. Goodnow. 1963. Brine migration in salt ice. In W. D. Kingery (ed.) Ice and Snow. M.I.T. Press, Cambridge, Massachusetts p. 237-247.
- Kolaian, J. H. and P. Low. 1963. Calorimetric determination of unfrozen water in montmorillonite pastes. Soil Science 9:376-384.
- Koopmans, R. W. R. 1965. Soil freezing and soil water characteristic curves. Ph.D. Thesis, Cornell University.
- Lewis, E. L. and E. R. Walker. 1970. The water structure under a growing sea ice sheet. Journal of Geophysical Research 75:6836-6845.
- Mahendrappa, M. K. 1969. Determination of nitrate nitrogen in soil extracts using a specific ion activity electrode. Soil Science 108:132-136.
- Murrmann, R. P. and P. Hoekstra. 1970. Effect of thermal gradient on ionic diffusion in frozen earth materials, Part I: Experimental Research Report 284, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
- Murrmann, R. P., P. Hoekstra, and R. C. Bialkowski. 1968. Self-diffusion of sodium ions in frozen Wyoming bentonite-water pastes. Soil Science Society of America Proceedings 32:501-506.
- Neriseova, Z. A. and N. A. Tsytoich. 1963. Unfrozen water in frozen soils: In N. A. Tsytoich (ed.) Contributions by the Russian delegation to the International Conference on Permafrost. Published by Academy of Science, USSR Moscow, 1963. English Translation in International Conference on Permafrost, Proc. First NRC-NAS Pub. No. 1287 p. 230-234.
- Nielson, D. R., R. D. Jackson, J. W. Cary, and D. D. Evans. 1970. Soil water. Western Regional Research Technical Committee W-68. Water movement in soils. 267 p.

- Oien, A. and A. R. Selmer-Olsen. 1969. Nitrate determination in soil extracts with the nitrate electrode. *Analyst* 94:888-894.
- Onken, A. B., H. D. Sunderman, and R. Jones. 1970. Use of the nitrate electrode for determination of nitrates in soils of the Texas High Plains. Texas Agricultural Experiment Station Report No. 2767, College Station, Texas.
- Porter, L. K., W. D. Kemper, R. D. Jackson, and B. A. Stewart. 1960. Chloride diffusion in soils as influenced by moisture content. *Soil Science Society of America Proceedings* 24:460-463.
- Potterton, S. S. and W. D. Shults. 1967. An evaluation of the performance of the nitrate selective electrode. *Analytical Letters* 1:11-22.
- Sartz, R. S. 1968. Soil water movement as affected by deep freezing. Presented at Division S-1 Symposium on Freezing and Thawing Phenomenon in Soils, American Society of Agronomy, New Orleans, Louisiana.
- Snowdon, P. N. and J. C. R. Turner. 1960. The Sorst Effect in some 0.01 normal aqueous electrolytes. *Transactions of the Faraday Society* 56:1409-1418.
- Thomas, G. W. and A. R. Swoboda. 1970. Anion exclusion effects on chloride movement in soils. *Soil Science* 110:163-166.
- Van Schaik, J. C. and W. D. Kemper. 1966. Chloride diffusion in clay-water systems. *Soil Science Society of America Proceedings* 30:22-25.
- Willis, W. O., C. W. Carlson, J. Alessi, and H. J. Haas. 1961. Depth of freezing and spring runoff as related to fall moisture level. *Canadian Journal Soil Science* 41:115-123.
- Willis, W. O., H. L. Parkinson, C. W. Carlson, and H. J. Haas. 1964. Water table changes and soil moisture loss under frozen conditions. *Soil Science* 98:244-248.

APPENDIX A

Analysis of variance and tables of means for Exp. A-1.

a. Analysis of variance table.

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
D	17	4136711.00	★ ★
R	2	788.01	
DR	34	1492.03	
F	1	92.96	ns
DF	17	300685.68	★ ★
RF	2	1501.13	
DRF	34	2413.47	
M	1	309.33	ns
DM	17	90355.75	★ ★
RM	2	1274.00	
DRM	34	399.17	
FM	1	6.85	ns
DFM	17	118980.06	★ ★
RFM	2	9960.36	
DRFM	34	3061.54	
TOTAL	215		

where D = depth, R = replication, F = frozen or non-frozen, M = moisture content, ★ ★ = significant at the 0.01 level, and ns = not significant.

b. Percent water in frozen cores.

Depth(cm)	Moisture level	
	Saturated	Unsaturated
1-2	19.4	11.8
17-18	18.5	8.3

c. Means (ppm NO₃-N) of the D main effect and DF, DM, and DFM interactions.

Depth Increment	D	DF		DM		DFM			
	D	Frozen (F)	Non-frozen (N)	Saturated (S)	Unsaturated (U)	FS	FU	NS	NU
1	2480	1880	3080	2800	2165	2580	1190	3020	3140
2	619	703	534	659	579	758	648	559	510
3	190	363	17.4	116	265	204	521	26.6	8.21
4	128	254	2.54	44.9	212	87.1	421	2.77	2.50
5	87.3	172	2.50	7.57	167	12.4	332	2.50	2.50
6	65.4	128	2.50	4.53	126	6.38	250	2.50	2.50
7	52.5	102	2.50	2.50	103	2.50	203	2.50	2.50
8	23.8	45.1	2.50	2.50	45.1	2.50	88.0	2.50	2.50
9	11.1	19.7	2.50	2.50	19.7	2.50	37.1	2.50	2.50
10	2.79	3.07	2.50	2.50	3.08	2.50	3.83	2.50	2.50
11	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
12	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
13	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
14	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
15	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
16	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
17	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
18	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50

where depth-increment 1 = 0-1 cm, 18 = 17-18 cm.

S \bar{x} for DFM = 32

d. Depth of freezing and length of freezing time.

Time (hrs)	Depth frozen (cm)	
	Saturated	Unsaturated
5	8.5	9.4
10	10.7	11.6
15	12.1	13.0
20	18.0	18.0

APPENDIX B

Analysis of variance and table of means for Exp. A-2.

a. Analysis of variance table.

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
D	17	99871.50	* *
B	1	85161.06	ns
DB	17	66994.18	*
S	2	9520.89	ns
DS	34	17023.09	ns
BS	2	36583.03	ns
DBS	34	31879.50	
TOTAL	107		

where D = depth, B = block (position), S = number of cycles, * = significant at the 0.05 level, * * = significant at the 0.01 level, and ns = not significant.

b. Nitrate-difference (frozen-unfrozen) means (ppm $\text{NO}_3\text{-N}$) of the D main effect and DB interaction.

Depth Increment	D	DB	
		Top Block	Bottom Block
1	452	10.0	895
2	-208	-297	-121
3	-167	-159	-176
4	-78.8	-87.8	-69.7
5	-7.65	-3.78	-11.5
6	-16.9	0.98	-34.7
7	0.39	1.23	-0.43
8	1.32	1.32	1.32
9	0.41	0.39	0.43
10	0.69	0.94	0.44
11	0.75	1.46	0.04
12	0.55	0.99	0.11
13	0.38	0.31	0.44
14	0.50	0.90	0.10
15	0.33	0.64	0.02
16	0.44	0.76	0.12
17	1.11	1.12	1.09
18	0.71	1.11	0.32

where depth-increment 1 = 0-1 cm, 18 = 17-18 cm.

$S\bar{x} = 103$

APPENDIX C

Analysis of variance for Exp. A-4.

a. Analysis of variance table.

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVELS OF SIGNIFICANCE
S	1	119633.87	*
F	1	189754.87	ns
SF	1	18149.29	ns
R	1	1590.36	
SR	1	626.08	
FR	1	31685.23	
SFR	1	637.60	
D	16	1371982.00	**
SD	16	27728.27	**
FD	16	76381.68	**
SFD	16	4405.29	**
RD	16	423.48	
SRD	16	2404.14	
FRD	16	15462.07	
SFRD	16	1134.26	
O:SFRD	136	129.20	
TOTAL	271		

where S = moisture content, F = soil sampled after freezing or thawing, R = replication, D = depth from freezing front, O = observations, ns = not significant, * = significant at the 0.05 level, and ** = significant at the 0.01 level.

APPENDIX D

Analysis of variance and table of means for Exp. A-4.

a. Analysis of variance for data presented in Fig. 19.

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
R	2	2334.05	
D	9	5623154.00	* *
RD	18	7994.00	
S	6	8380.26	*
RS	12	1890.95	
DS	54	186150.43	* *
RDS	108	5044.57	
TOTAL	209		

where R = replications, D = depth, S = soil, * = significant

at the 0.05 level, and * * = significant at the 0.01 level.

b. Analysis of variance for data presented in Table 3.

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
S	6	0.1442	* *
ERROR	14	0.0037	
TOTAL	20		

where S = soil and * * = significant at the 0.01 level.

c. Means (ppm $\text{NO}_3\text{-N}$) of the DS interaction (also presented in Fig. 19).

Depth Increment	Soil						
	CK2	NK2	CKS	CM2	CMS	NM2	LS
1	1180	1167	1330	1470	1374	2220	2850
2	720	845	676	816	848	420	25.6
3	406	500	543	441	295	30.4	10.0
4	241	197	257	81.3	62.7	10.4	10.0
5	195	68.2	173	27.0	14.4	10.3	10.0
6	85.0	28.4	44.2	12.3	13.0	14.7	10.0
7	37.7	18.9	15.3	11.7	11.5	12.4	10.0
8	18.2	14.3	11.0	13.5	12.9	10.0	10.0
9	13.8	14.0	10.7	11.3	12.1	10.1	10.0
10	17.4	10.8	10.4	16.7	12.6	10.1	10.0

where depth-increment 1 = 0-1 cm 10 = 9-10 cm,

C = calcium saturated, N = sodium saturated, K = kaolinite clay,

M = montmorillonite clay, L = sand, 2 = moisture level at 20%, and

S = moisture level at saturation.

$\bar{Sx} = 18.6$.

APPENDIX E

Analysis of variance for Exp. A-5.

a. Analysis of variance.

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
P	1	1255.17	ns
R	1	3.15	
PR	1	36951.83	
D	4	1561916.00	* *
PD	4	46116.18	ns
RD	4	975.02	
PRD	4	13614.89	
S	2	18732.33	ns
PS	2	2361.26	ns
RS	2	3896.00	
PRS	2	10862.54	
DS	8	7541.92	ns
PDS	8	12293.92	* *
RDS	8	4233.19	
PRDS	8	1831.68	
O:PRDS	60	445.58	
TOTAL	119		

where P = position (nitrates added to the warm or cold end), R = replication, D = depth, S = soil, ns = not significant, and * * = significant at the 0.01 level.

APPENDIX F

Analysis of variance and table of means for Exp. B-1.

a. Analysis of variance.

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
D	16	324.33	ns
R	2	2043.06	
DR	32	4592.33	
N	2	383807.81	* *
DN	32	13549.83	* *
RN	4	17235.12	
DRN	64	2854.50	
C	1	143638.25	ns
DC	16	6567.35	* *
RC	2	77884.62	
DRC	32	1105.68	
NC	2	129659.81	ns
DNC	32	5067.95	*
RNC	4	30759.71	
DRNC	64	2090.21	
TOTAL	305		

where D = depth, R = replication, N = applied nitrate before or after the soils were frozen or no nitrate application, C = core or field plot, ns = not significant, * = significant at the 0.05 level, and * * = significant at the 0.01 level.

b. Means (ppm $\text{NO}_3\text{-N}$) of the DN interaction.

Depth Increment	Nitrate application treatments		
	No Nitrates Applied	Nitrates Applied Before Freeze	Nitrates Applied After Freeze
1	22.8	24.9	165
2	16.5	29.9	173
3	13.2	31.3	176
4	7.28	35.9	175
5	6.04	41.9	162
6	5.27	51.9	173
7	4.89	63.5	171
8	4.82	80.8	157
9	4.23	91.9	132
10	4.79	94.7	115
11	5.69	112	113
12	5.13	122	90.7
13	4.67	120	80.2
14	8.72	115	74.1
15	10.3	132	59.8
16	15.7	159	76.1
17	18.8	148	65.8

where 1 = 0-1 cm and 17 = 16-17 cm.

$\bar{Sx} = 21.8$.

APPENDIX G

Analysis of variance and tables of means for Exp. B-2.

a. Analysis of variance for part (a).

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
D	5	5741971.00	**
R	1	110690.43	
DR	5	192591.50	
T	1	257280.06	ns
DT	5	812233.00	ns
RT	1	245639.31	
DRT	5	164589.37	
M	2	201901.31	ns
DM	10	167044.56	ns
RM	2	61440.12	
DRM	10	217919.50	
TM	2	264474.75	ns
DTM	10	171135.00	ns
RTM	2	218491.31	
DRTM	10	163374.25	
S	2	151433.50	ns
DS	10	189911.25	ns
RS	2	254082.12	
DRS	10	181607.00	
TS	2	185132.81	ns
DTS	10	182135.00	ns
RTS	2	199623.00	
DRTS	10	166931.68	
MS	4	263709.25	ns
DMS	20	207520.50	ns
RMS	4	238878.12	
DRMS	20	165729.37	
TMS	4	145088.00	ns
DTMS	20	211678.00	ns
RTMS	4	155266.06	
DRTMS	20	186240.50	
TOTAL	215		

where D = depth, R = replication, T = time of application, M = moisture content, S = soil, ns = not significant and ** = significant at the 0.01 level.

b. Means (ppm $\text{NO}_3\text{-N}$) of the DT interaction for part (a).

Depth Increment	Time of Application	
	Applied After Freeze	Applied Before Freeze
1	1370	862
2	360	818
3	78.5	307
4	43.6	149
5	23.1	60.3
6	18.2	10.0

where depth-increment 1 = 0-3 cm 6 = 15-18 cm.

$\overline{Sx} = 96.$

c. Analysis of variance for part (b).

SOURCE OF VARIATION	DEGREES OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
D	5	6222336.00	* *
R	1	43112.92	
DR	5	16771.19	
P	1	2104.77	ns
DP	5	392.54	ns
RP	1	10300.37	
DRP	5	37065.28	
T	1	210.62	ns
DT	5	566812.75	* *
RT	1	49533.53	
DRT	5	13414.18	
PT	1	83988.50	ns
DPT	5	20318.48	ns
RPT	1	1151.99	
DRPT	5	27136.50	
M	1	2426.04	ns
DM	5	4583.55	ns
RM	1	43720.37	
DRM	5	20139.79	
PM	1	5791.35	ns
DPM	5	21277.44	*
RPM	1	2201.15	
DRPM	5	2365.23	

c. Continued

SOURCE OF VARIATION	DEGREE OF FREEDOM	MEAN SQUARES	LEVEL OF SIGNIFICANCE
TM	1	370.41	ns
DTM	5	11398.98	ns
RTM	1	27305.89	
DRTM	5	9392.82	
PTM	1	4632.47	ns
DPTM	5	5245.55	ns
RPTM	1	12152.52	
DRPTM	5	6879.76	
S	1	80232.81	ns
DS	5	4451.30	ns
RS	1	2663.35	
DRS	5	15627.29	
PS	1	10678.84	ns
DPS	5	13019.04	ns
RPS	1	45531.53	
DRPS	5	33579.39	
TS	1	635.47	ns
DTS	5	13122.78	*
RTS	1	382.22	
DRTS	5	2449.39	
PTS	1	723.45	ns
DPTS	5	4326.46	ns
RPTS	1	496.33	
DRPTS	5	6083.95	
MS	1	21971.41	ns
DMS	5	6028.98	ns
RMS	1	893.12	
DRMS	5	41336.76	
PMS	1	4325.33	ns
DPMS	5	2630.54	ns
RPMS	1	65656.43	
DRPMS	5	11905.71	
TMS	1	31250.33	* *
DTMS	5	15608.63	ns
RTMS	1	16.86	
DRTMS	5	41383.19	
PTMS	1	6.19	ns
DPTMS	5	1815.71	ns
RPTMS	1	15324.16	
DRPTMS	5	11361.70	
TOTAL	191		

where D = depth, R = replication, P = position, T = time of application, M = moisture content, S = soil, ns = not significant, * = significant at the 0.05 level, and * * = significant at the 0.01 level.

- d. Representative temperature profiles (degrees centigrade) for a bare Vienna-loam soil.

Date of day-time soil temperatures			
Depth (cm)	Oct. 31, 1971	Jan. 8, 1972	March 5, 1972
1	4.1	-1.1	-3.7
5	2.9	-1.2	-3.6
10	2.5	-0.6	-2.4
15	2.9	-0.2	-2.2
20	4.7	0	-1.6
30	5.8	0.4	-1.1
50	7.8	1.7	0
70	9.4	2.2	0.4
100	10.6	3.3	0.9
160	11.4	5.0	2.2
